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Contributions from the Sheffield Laboratory of Yale University.

THE DOUBLE AMMONIUM LEAD CHLORIDES.[1]

BY H. W. FOOTE AND L. H. LEVY.

These experiments were undertaken to determine the double ammonium lead chlorides capable of forming at 25°. We used the solubility method[2] which has already been applied to several series of double salts.

André[3] described a number of double ammonium lead chlorides which were shown not to exist by Randall[4] and by Wells and Johnston[5] in papers which appeared at about the same time. Randall described instead the 2 salts:

$$2NH_4Cl.PbCl_2$$
$$NH_4Cl.2PbCl_2$$

[1] NOTE—Having carefully followed the work described in this article, and having compared the products obtained with our original sample of the supposed salt $NH_4Cl.PbCl_2.H_2O$ made by Wells and Johnston, I am fully convinced that the latter was not a pure product, but $NH_4Cl.2PbCl_2$ contaminated with ammonium chloride and mother liquor. The molecular weight of NH_4Cl is so small in comparison with that of $PbCl_2$ that a moderate amount of such contamination led to mistaken conclusions.
H. L. WELLS.

[2] THIS JOURNAL, **30**, 330 (1903).
[3] Compt. rend., **96**, 435 (1883).
[4] THIS JOURNAL, **15**, 494 (1893).
[5] Am. J. Sci., **46**, 25 (1893).

and Wells and Johnston the salts:

$$NH_4Cl.PbCl_2.H_2O.$$
$$NH_4Cl.2PbCl_2.$$

It will be noticed that the 1:2 salt was found by both Randall and Wells and Johnston, but there is a disagreement in regard to the other 2 salts.

In our experiments, weighed quantities of ammonium chloride and lead chloride were treated with a known quantity of water, the mixtures heated and then allowed to crystallize. They were shaken, usually for several days, in the thermostat, at 25°. At the ammonium end of the series, the mixed salts were entirely dissolved when heated. At the lead end this could not be done, but the thorough shaking insured equilibrium. Both solutions and residues were analyzed. The solutions were drawn into a pipette, through a filter of glass wool and weighed. The pipette was first warmed slightly to prevent crystallization on the walls. The residue in the bottles was removed as quickly as possible and dried between filter paper. Ammonia was determined by distilling with sodium hydroxide and passing the distillate into a known amount of standard hydrochloric acid. The excess of acid was titrated by means of a standard solution of ammonia. Lead was determined by adding a little nitric acid, to dissolve all lead chloride, and then 10 cc. of sulphuric acid, the solution being subsequently evaporated on a steam-bath to sulphuric acid. The lead sulphate, after treating with a small amount of water, was filtered on a Gooch crucible, washed with a very dilute solution of sulphuric acid, ignited and weighed. The results of the analyses of both solutions and residues follow:

Table I.—Solubility of Ammonium and Lead Chlorides at 25°.

	Per cent NH_4Cl in sol.	Per cent $PbCl_2$ in sol.	Per cent NH_4Cl in res.	Per cent $PbCl_2$ in res.	Composition of residue.
1.	28.41	1.17	95.06	3.22	$NH_4Cl + NH_4Cl.2PbCl_2$
2.	27.89	1.22	50.80	47.70	" "
3.	27.71	0.99	12.30	87.04	" "
4.	27.45	0.93	10.27	88.61	$NH_4Cl.2PbCl_2$
5.	26.25	0.75	10.24	89.04	"

Table I—(continued).

	Per cent NH_4Cl in sol.	Per cent $PbCl_2$ in sol.	Per cent NH_4Cl in res.	Per cent $PbCl_2$ in res.	Composition of residue.	
6.	*24.69*	*0.85*	*10.46*	*88.74*	$NH_4Cl.2PbCl_2$	
7.	*21.59*	*0.35*	*10.56*	*88.42*	"	
8.	*17.97*	*0.29*	*9.62*	*89.92*	"	
9.	*13.51*	*0.17*	*8.93*	*90.76*	"	
10.	*11.47*	*0.12*	*8.71*	*90.88*	"	
11.	*10.25*	*0.11*	*8.52*	*91.20*	"	
	Calculated,		8.78	91.22		
12.	2.71	0.06	7.30	92.60	$NH_4Cl.2PbCl_2 + PbCl_2$	
13.	2.81	0.04	7.24	92.70	"	"
14.	2.78	0.01	5.87	93.72	"	"
15.	2.79	0.02	1.51	98.22	"	"

These solubility results are not entirely satisfactory in every respect, but they prove certain points. In Nos. 1–3 the solubility remains practically constant, showing that the same salts are present in the residue. As the residues vary from 95.06–12.30 per cent of ammonium chloride, it is evident that the 2 : 1 salt and the 1 : 1 : 1 could not have formed, as the latter contains 15.32 per cent of ammonium chloride. Had either of these formed, the solubility results in Nos. 1 and 2 would have differed from No. 3. In these experiments, there was evidently a mixture of ammonium chloride and a double salt containing less than 12 per cent of ammonium chloride.

Experiments 12–15 also have constant solubility and show that mixtures were present containing lead chloride and a double salt with more than 7.3 per cent of ammonium chloride.

Nos. 4–11 show widely varying solubility, indicating the presence of a pure double salt, but the residues are not constant in composition, varying from 10.27 to 8.52 per cent of ammonium chloride.

We were at first inclined to believe from the results that 2 salts were present, the 1 : 2, which was described before, and also a salt having the composition $3NH_4Cl.5PbCl_2$. The latter salt would contain 10.36 per cent of ammonium chloride. Subsequent results showed that but one salt was present.

The residues were always very fine and it was not easy to dry them rapidly between filter paper. Any mother liquor drying

on the salt would tend to increase the percentage of ammonium chloride in the residue, and this would be more noticeable when the solutions were at the ammonium end of the series. The crystals may have also included a small amount of mother liquor, which would tend to increase the percentage of ammonium chloride found.

In deciding what salt was present in Experiments 4–11 of the preceding table, we proceeded as follows: Two solutions were prepared from calculated amounts of ammonium chloride, lead chloride and water, so that a small quantity of crystals would separate at 25° from one solution near the ammonium end of the series and from the other solution near the lead end. The necessary charges were calculated from the solubility results previously given. The quantities of salts and water used were the following:

I. Ammonium end.		II. Lead end.	
501 grams	NH_4Cl	160 grams	NH_4Cl
25.86 "	$PbCl_2$	6.56 "	$PbCl_2$
1483 cc.	H_2O	1838 cc.	H_2O

The salts were completely dissolved in the water by heating the mixtures. The solutions were placed in a thermostat at 25° and allowed to crystallize. The crystals from solution I were larger than those from solution II. Some of them from each solution were examined by Professor S. L. Penfield a few months before his death. The crystals were not sufficiently well formed to allow of accurate optical measurements. They both, however, were similar in form and habit and had identical optical properties, so far as these could be distinguished, so that the same salt was evidently present in each case.

For analysis, the crystals were removed from the solutions and dried rapidly between filter paper. The same methods of determination were used as before. The following results were obtained:

	I.	II.	Calculated for $NH_4Cl.2PbCl_2$.	Calculated for $3NH_4Cl.5PbCl_2$
$PbCl_2$	90.09 ; 89.94 ; 89.96	90.50	91.22	89.64
NH_4Cl	. . . . .	9.68 ; 9.67	8.78	10.36

The results are not as close as could be desired, coming between the theoretical percentages for the 1 : 2 and the 3 : 5. As the solutions contained a large excess of ammonium chloride, the ammonium would tend to come high in the analyses and the lead correspondingly low, so there can be no doubt that the salt present in each case was $NH_4Cl.2PbCl_2$, which has previously been described.

An attempt was now made to prepare the 2 : 1 salt according to Randall's directions. Two hundred and fifty cc. of ammonium chloride solution, saturated in the cold, were raised to the boiling point and 15 grams of lead chloride added. This did not all dissolve and 50 cc. of ammonium chloride were added and the solution heated, after which the solution cleared. The beaker, containing this solution, was set aside to cool, by placing it within another beaker and surrounding it with cotton waste. After some days the beaker was removed and 2 layers of crystals were noticed. Portions of both these layers were removed and ammonia determined. The results were:

	Per cent NH_4Cl.
Upper layer	65.35
Lower layer	20.78
Calculated for 2 : 1 salt	27.82

Experiments were also carried on to ascertain if another double salt formed at a different temperature. A mixture of the 1 : 2 salt and ammonium chloride was placed in a dilatometer and readings taken from 0°–70°, but no irregular change in volume was observed, making it very probable that only the one double salt forms in the range of temperature investigated.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
October, 1906.

Contributions from the Sheffield Laboratory of Yale University.

THE DOUBLE CAESIUM LEAD BROMIDES.

By H. W. Foote.

The double caesium lead bromides have been described by Wells and Walden.[1] They are the following:

$$CsPb_2Br_5$$
$$CsPbBr_3$$
$$Cs_4PbBr_6.$$

The salt $CsPbBr_3$ was described as occurring in 2 different forms, one white and the other orange-colored. The white form passed into the orange when heated, but the reverse change did not take place upon cooling. The orange form was prepared under a wide range of conditions, while the white form was obtained only from solutions containing but little caesium bromide.

In the present article, the conditions of formation of the 3 salts have been determined at 25°, by the solubility method, chiefly with the object of ascertaining whether or not both forms of the 1 : 1 salt could be obtained at this temperature by varying the proportions of caesium and lead bromides in solution. Only the orange form could be isolated, however, and the white form is, apparently, unstable at this temperature.

Lead bromide was prepared by precipitating a solution of lead nitrate with pure hydrobromic acid; caesium bromide, by dissolving very pure caesium carbonate in hydrobromic acid and evaporating to dryness.

The experiments were carried out as described in the preceding article. As it was feared that lead bromide might hydrolyze and form a basic bromide, a very dilute solution of hydrobromic acid was used as solvent instead of pure water. This solution contained 0.1906 gram of hydrobromic acid in 25 cc.

Solutions and residues were analyzed by dissolving in water with the addition of nitric acid, when necessary to complete the solution, adding a slight excess of sulphuric acid and evaporating till water was removed. The residue was treated with a tle water, and lead sulphate filtered on a Gooch crucible

[1] Am. J. Sci., 45, 121 (1893).

when it was present in appreciable amount. The solutions usually contained too small an amount of lead to weigh. The solution containing caesium sulphate and sulphuric acid was evaporated and heated and the normal sulphate obtained by igniting several times gently with ammonium carbonate. As the residues were anhydrous, lead alone was determined in most cases and caesium calculated by difference.

The results obtained are given in Table I. Italics are used when a double salt was present, as shown by varying solubility and constant composition of the residue.

Table I.—Solubility of Caesium Lead Bromides at 25°.

No.	Per cent CsBr in solution.	Per cent $PbBr_2$ in solution.	Per cent CsBr in residue.	Residue contains :
1.	0.24	0.33	6.62	$PbBr_2$ and $CsPb_2Br_5$
2.	0.33	0.36	18.93	
3.	*12.83*	trace	*23.50*	$CsPb_2Br_5$
4.	*17.24*	"	*22.94*	
	Calculated for $CsPb_2Br_5$		22.49	
5.	17.68	trace	27.57	$CsPb_2Br_5$ and $CsPbBr_3$
6.	17.82	"	31.72	
7.	*18.58*	"	*36.21*	$CsPbBr_3$
8.	*19.57*	"	*36.51*	
9.	*33.65*	"	*37.89*	
	Calculated for $CsPbBr_3$		36.72	
10.	36.53	trace	38.00	$CsPbBr_3$ and Cs_4PbBr_6
11.	36.57	"	39.80	
12.	37.18	"	48.37	
13.	36.89	"	65.54	
14.	*46.40*	"	*70.58*	Cs_4PbBr_6
15.	*51.15*	"	*70.27*	
	Calculated for Cs_4PbBr_6		69.89	
16.	54.71	trace	74.92	Cs_4PbBr_6 and CsBr
17.	54.16	"	98.41	
18.	55.23	none	100	CsBr

The residues in Nos. 7–9 were deep orange, while the mixtures on either side were lighter in color, due to the presence of the other salts. The white form of this salt was never observed and it would appear to be unstable at this temperature.

The residues in Nos. 14–15 were light salmon in color instead

of white. That this is the natural color of the 4: 1 salt instead of being due to the presence of a trace of the 1: 1 was shown by the fact that the mixture of this salt with caesium bromide was also slightly colored.

SHEFFIELD LABORATORY,
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THE ABSORPTION SPECTRA OF CERTAIN SALTS IN AQUEOUS SOLUTION AS AFFECTED BY THE PRESENCE OF CERTAIN OTHER SALTS WITH LARGE HYDRATING POWER.

BY HARRY C. JONES AND HORACE S. UHLER.

(SEVENTEENTH COMMUNICATION.)

[This investigation was carried out with the aid of a grant from the Carnegie Institution.]

The importance of the absorption spectra of salts as affected by the presence of certain other salts, in their bearing on the hydrate theory as proposed hy Jones, has already been pointed out.[1] It has been mentioned that our attention was directed to certain of these color changes by Dr. Lewis.

The chief reactions that we have studied are those between cobalt chloride, copper chloride and copper bromide, when treated with calcium chloride, calcium bromide, or aluminium chloride. It is well known that aqueous solutions of cobalt chloride are purplish-red in color. When a strong, aqueous solution of cobalt chloride is treated with a fairly concentrated, aqueous solution of calcium chloride, the color of the cobalt solution is changed from purplish-red to blue. This same result is obtained if calcium bromide is used instead of calcium chloride.

Similar color changes result when solutions of aluminium chloride are added to solutions of cobalt chloride. Indeed, smaller amounts of aluminium chloride are required to affect the same color changes, than are necessary when either of the salts of calcium is used.

[1] THIS JOURNAL, 34, 291 (1905). J. Chim. physik., 3, 494 (1905).

If any one of the above-named dehydrating agents is added to a fairly dilute solution of cupric chloride or bromide, marked color changes result. A fairly concentrated solution of cupric chloride or bromide is greenish-brown, while dilute solutions are blue. As more and more water is added to the more concentrated solutions, we have all gradations between the above colors. The addition of calcium chloride, calcium bromide, or aluminium chloride to a blue solution of the copper salt, changes the color to green, and if sufficient of the dehydrating agent is added the color becomes greenish-brown.

In the present investigation these color changes have been studied quantitatively. The absorption spectra of the substances separately, and when mixed in known quantities, have been observed by means of a direct-reading spectroscope, and the wave lengths of the absorption bands read off and recorded.

What is of far greater importance, however, is the photographic record of such absorption bands, and the changes in the position of these bands as varying amounts of one or another dehydrating agent is added to the salt in question. These photographs have been taken by means of the spectrograph to be described later in this paper.

Before taking up in detail the work which is here recorded, a brief discussion of some of the more important investigations in this same field seems desirable.

The fact that dehydrating agents produce the change in color from purplish-red to blue, and, further, that the same color change is effected by raising the temperature of the solution, early suggested the view that the change in color from reddish to blue was due to a loss of water on the part of the salt in solution.

Babo[1] observed that cobalt chloride, in concentrated solution, was colored blue by absolute alcohol, at ordinary temperatures. At more elevated temperatures a few drops of alcohol are sufficient to produce the blue color. A solution of calcium chloride or magnesium chloride changes the color of cobalt chloride to blue very readily, especially at the boiling points of the solu-

[1] Ber über d. Verhand. d. Gesell. f. Beford. d. Naturw. zu Freiburg, i. B. 1857, Nr. 17, 283. Jahres. d. Chem., 1857, 72.

tions. A saturated solution of sodium chloride will also produce the blue color at elevated temperatures.

A concentrated solution of zinc chloride, on the other hand, gives only a red color with cobalt chloride, even when the mixture is warm. Babo thinks that this is due to the formation of a double salt. He concludes that whenever there is a transformation from the reddish to the blue color, there is a dehydration of the cobalt salt.

Gladstone,[1] in his well-known paper "On the Use of the Prism in Qualitative Analysis," takes up the question here under discussion. In connection with salts of cobalt he says: "We are accustomed to speak of blue and red salts of cobalt, but this difference depends really on the state of hydration, and the prism reveals an analogy otherwise unsuspected between the two colors."

Gladstone points out that the salts of cobalt, in general, when anhydrous, are blue, and that the hydrated salts or aqueous solutions are red. The only exception seems to be the sulphocyanate, whose saturated aqueous solution is blue. The dilute aqueous solution of even this salt is, however, red.

Gladstone,[2] in his subsequent investigations with the *isoscope*, comes essentially to the same conclusions as those pointed out above. He brought within the scope of this investigation a large number of colored compounds. Among the substances where the character of the color changes with the dilution, are the 3 salts upon which special stress has been laid in this investigation—cobalt chloride, copper chloride and copper bromide.

In 1859 Schiff[3] published a paper on the "Effect of Rise in Temperature on the Intensity of the Color of Solutions," in which such questions as those now under consideration were discussed. He added a number of cases of color changes with change of temperature to those already observed by Babo and Gladstone, and seems to be of the same general opinion as to their cause—that there is a change in the magnitude of the hydration.

[1] J. Chem. Soc., **12**, 79 (1858).
[2] *Ibid.*, **11**, 36 (1859).
[3] Ann. Chem. (Liebig), **110**, 203 (1859).

Bersch,[1] in 1867, proposed a new view to account for the color changes in the case of cobalt salts. He recognized that when $CoCl_2.6H_2O$ is heated it yields two well-defined compounds, $CoCl_2.4H_2O$ and $CoCl_2.2H_2O$, the former being bluish-red and the latter violet in color.

He, however, thought that he established the fact that the compound $CoCl_2.6H_2O$ may become blue without loss of water. He concluded, therefore, that there are two modifications of the compound $CoCl_2.6H_2O$—the one red and the other blue—and that the first change in color on heating is due to the transformation of the red into the blue modification.

Tichborne[2] called attention to an interesting and important fact which is stated in his own words: "It is easy to portend that although impossible at ordinary atmospheric pressure, and in an ordinary aqueous solution, to dissociate the water, it is only necessary to boil such a solution under sufficient amount of pressure to obtain the thermoanalytic point. This was demonstrated by the following experiment: A weak solution of chloride of cobalt was sealed up in a glass tube, two-thirds of the capacity of which was empty. On boiling the liquid in this tube the solution gradually passes with the increment of heat through all the shades of purple, until the contents ultimately become pure blue. Thus, in this aqueous solution we have attained, by extraordinary pressure, the temperature necessary for the separation of the water. The change of color may be easily observed as it occurs in the capillary tube, by holding any white material at the back of the tube and opposite the experimenter." It is obvious that this observation is of importance in connection with the theory as to the cause of these color changes.

Attention was again called to this same fact by Clowes[3] about 2 years later.

The spectrum of cobalt chloride was early studied, especially by Vogel.[4] He pointed out that the red, aqueous solution of cobalt chloride shows only one broad band in the green,

[1] Sitzung. Wien., II. **56**, 726 (1867).
[2] Chem. News, **28**, 133 (1872).
[3] *Ibid.*, **29**, 161 (1874).
[4] Ber. d. chem. Ges., **11**, 913 (1878).

and this lies between F and D. In stronger solutions there is absorption of the violet, blue and green, only the region to the right of these being transparent.

When the solution of cobalt chloride is evaporated nearly to dryness it becomes blue. The absorption of the blue and green completely disappears, and 2 sharp bands manifest themselves in the red and orange. Vogel also studied the spectrum of the blue, alcoholic solution, and pointed out certain relations between it and the spectrum of the blue, aqueous solution. He observed, however, that the absorption bands are closer to the red in the aqueous than in the alcoholic solution.

Russell[1] made a fairly extended spectroscopic study of solutions of cobalt chloride. He worked with a fused salt, with its solution in concentrated hydrochloric acid, and with its solution in various alcohols. He showed that the spectrum in the concentrated acid was very similar to that of the fused salt, the two bands being shifted a little towards the blue.

The spectrum of cobalt chloride, when dissolved in the various alcohols and in glycerin, was practically the same, independent of the nature of the solvent.

Russell also worked with aqueous solutions at different concentrations and studied their absorption spectra. He likewise studied the effect of change of temperature on the various aqueous solutions. He concluded that the color of the aqueous solutions was due to the presence of hydrates in these solutions.

Potilitzin[2] took up the study of cobalt chloride especially to test the conclusions reached by Bersch—that there are 2 modifications of the compound $CoCl_2.6H_2O$, the one red and the other blue.

Potilitzin showed that when the hexahydrate is warmed to about 52°, for 4 hours, it passes over into the dihydrate, $CoCl_2.2H_2O$, which is reddish, with a slightly violet tint. The same compound is obtained when the hexahydrate is placed in a desiccator for a few days. At 100° the dihydrate passes over into the monohydrate, $CoCl_2.H_2O$, which is dark violet in color.

[1] P. Roy. Soc., **32**, 258 (1881).
[2] Ber. d. chem. Ges., **17**, 276 (1884).

When the monohydrate is warmed from 110°–120°, it loses its last molecule of water and yields the anhydrous salt, which is blue.

Potilitzin concludes that the transition temperatures from one hydrate to another of cobalt chloride, as given by Bersch, are in error; that there is only one modification of the compound $CoCl_2.2H_2O$, and that the only other hydrate of cobalt chloride has the composition $CoCl_2.H_2O$.

The formation of blue cobalt chloride from red, by whatever means affected, is a dehydration process.

Sabatier[1] showed that hydrates of cobalt chloride containing less water than the hexahydrate, were formed when hydrochloric acid was added to a strong, aqueous solution of the cobalt salt. There seems to be some evidence of the formation of chlorhydrates.

He[2] performed similar experiments with copper chloride, and obtained analogous results.

In 1890 Lescoeur[3] took up a study of the hydrates formed by cobalt chloride. He found also that at 120° the compound $CoCl_2.2H_2O$ is produced. When any of the hydrates are heated up to 140° they yield the anhydrous chloride. The compound $CoCl_2.2H_2O$, of lilac color, is easily obtained by drying the hexahydrate over sulphuric acid, at the ordinary temperature. There is no intermediate hydrate such as $CoCl_2.4H_2O$ formed.

In 1891 a number of papers appeared bearing upon the problem under discussion. Étard[4] pointed out the importance of studying simultaneously the color changes and solubility curve. He worked with cobalt chloride and cobalt iodide, and showed that at those temperatures corresponding to the formation of a new hydrate the solubility curve changed direction, being no longer a straight line. The new hydrate would have a different solubility from the old, and this was clearly shown by the solubility curves. He thus proved the existence of the following hydrates:

$CoI_2.6H_2O$, $CoI_2.4H_2O$, $CoI_2.2H_2O$, $CoCl_2.6H_2O$, $CoCl_2.2H_2O$.

[1] Compt. rend., **107**, 42 (1888).
[2] *Ibid.*, **106**, 1724 (1888).
[3] Ann. Chim. Phys. [6], **19**, 547 (1890).
[4] Compt. rend., **113**, 699 (1891).

Potilitzin[1] came back to the problem of the change in the color of cobalt chloride, having published a paper 7 years earlier on this same subject. He points out that when crystals of $CoCl_2.6H_2O$ melt they form a deep violet colored liquid, which becomes more and more deeply blue. He also states that dehydrating substances, in general, produce the blue color. He concludes that these changes in color are due entirely to changes in the hydration of the cobalt chloride.

Charpy[2] studied the vapor-tension of solutions of cobalt chloride and plotted the results as curves. He found that the curve was made up of two well-defined, rectilinear portions. The two portions of the curves met at 75°. Above this temperature the solutions were blue in color.

This agrees, in a sense, with the results found by Étard. As Charpy points out, his results can be interpreted in either of two ways. There is either a change in the hydration of the salt with change in temperature, or there is a change in the state of molecular aggregation. From these results it is impossible to decide between the above two possibilities.

Wyrouboff[3] calls attention to the fact that the change in the color of solutions of cobalt chloride with rise in temperature, cannot be due to the presence of the anhydrous salt, since this combines with water with the greatest avidity, a large amount of heat being at the same time liberated. He showed that the change in color was due to the formation of the monohydrate, $CoCl_2.H_2O$, which is formed in larger and larger quantities the more elevated the temperature. This violet-colored hydrate is stable, not losing its molecule of water until a temperature of 140° is reached, when it passes over into the pale blue, anhydrous salt.

Engel[4] does not accept any of the theories that have been advanced to account for the color changes that take place in cobalt chloride. He reviews briefly our knowledge of the hydrates of cobalt chloride, and then takes up the theories that have been proposed to account for the color changes.

[1] Bull. Soc. Chim. [3], 6, 264 (1891).
[2] Compt. rend., 113, 794 (1901).
[3] Bull. Soc. Chim. [3], 5, 460 (1891).
[4] *Ibid.* [3], 6, 239 (1891).

He objects to the dehydration theory, that the blue color is due to the presence of the anhydrous salt, since this salt is light blue, while the solutions are much deeper blue, and, indeed, often indigo-blue. He objects to the theory of Wyrouboff, since the monohydrate is violet and never blue, and the solutions are often blue.

Engel does not believe that any general theory can be advanced to account for the changes in color which cobalt chloride undergoes. He thinks that each special case must be dealt with separately. He is of the opinion that the blue color is due to the presence of compounds which cobalt chloride is capable of forming with various substances. Some of these compounds are not blue, notably the one formed with zinc chloride; mercuric chloride, stannous chloride and the chloride of antimony behaved like the chloride of zinc.

Engel supports his theory that the blue color is due to the presence of double chlorides, by stating that he has obtained a double chloride of calcium and cobalt and calls attention to the fact that Chassevent[1] has prepared a blue double chloride of cobalt and lithium having the composition, $CoCl_2.LiCl.3H_2O$, which is probably analogous to $CoCl_2.HCl.3H_2O$, the compound formed with hydrochloric acid. The double copper salt is, however, red. Engel thinks that the blue color produced in a saturated solution by rise in temperature, is not due solely to the presence of the monohydrate, which is violet, but to the formation of a compound with hydrochloric acid, the hydrochloric acid being liberated as the result of the action of water on cobalt chloride.

Wyrouboff[1] answers a number of the objections advanced by Engel against the dehydration theory, especially concerning the color of the monohydrate. It is largely a question of physical state, whether we are dealing with transmitted or reflected light.

Le Chatelier[2] does not doubt the existence of blue double salts—chlorhydrates, alcoholates, etc.—but thinks the color changes can be easily explained on the dehydration theory.

[1] Bull. Soc. Chim. [3], 6, 3 (1891).
[2] *Ibid.* [3], 6, 3 (1891).

He points out that the formation of the acid chloride would involve also the formation of the oxychloride, which would be precipitated, and this is not the case.

Le Chatelier[1] shows that both red and blue cobalt chloride act on calcium carbonate, and that this and other lines of evidence adduced by Engel against the dehydrated theory are not valid.

Étard[2] studied the changes in the absorption spectra of cobalt chloride with change in temperature, and found, with rise in temperature, the disappearance of certain bands and the appearance of others. This work is analogous to that of Becquerel,[3] which deals especially with the absorption spectra of salts of didymium and uranium.

As Étard points out, the appearance of the new bands with rise in temperature shows that there is some new internal arrangement of the molecules, as we should expect if there was a change in the hydration as the temperature varies. As the nature of the molecules in the solution changes, new absorption bands will make their appearance.

The most elaborate work by far which has been done on the absorption spectra of cobalt salts is that of Hartley.[4] This is but part of an extensive investigation on the absorption spectra of a number of colored salts. The work includes also the chloride and bromide of copper.

The spectra of an aqueous solution of cobalt chloride, at temperatures ranging from 23° to 93°, were photographed and the bands also measured. Hartley concludes that his photographs of these spectra of the solution at different temperatures, show that the molecules of water are removed from the cobalt chloride with rise in temperature. The absorption bands widen in the red with rise in temperature, showing that the molecule is becoming simpler and vibrates in resonance with a larger number of waves.

Hartley worked also with solutions of cobalt chloride in absolute alcohol, at different temperatures, and concluded that

[1] Bul. Soc. Chim. [3], **6**, 84 (1891).
[2] Compt. rend., **120**, 1057 (1895).
[3] Ann. Chim. Phys. [6], **14**, 170 and 257.
[4] T. Roy. Soc. Dublin, II, **7**, 253 (1900).

rise in temperature did not affect the alcoholic solutions. He also worked with solutions of cobalt chloride in glycerin, with cobalt chloride mixed with hydrochloric acid, and with cobalt chloride to which a solution of calcium chloride had been added. Work similar to the above was done with cobalt bromide and iodide.

The effect of rise in temperature on the absorption spectra of a number of salts of chromium was also studied.

Hartley concludes that the effect of rise in temperature, in general, on the absorption spectra of solutions of salts is as follows: If the salts are anhydrous or not dehydrated at 100°, or if they do not change color when dehydrated, they do not change their absorption spectra when heated. Hydrated salts change their spectra with change in temperature, and this change is usually very nearly the same as that effected by dehydrating agents.

Ostwald[1] concludes that the red color of solutions of cobalt salts, in general, is due to the cobalt ion. He points out that the hexahydrate easily loses water and forms lower hydrates, which are blue in color. If the concentrated aqueous solutions are heated they turn blue. This same color change is very easily produced by adding to the solution of cobalt chloride chlorine ions. Thus the presence of hydrochloric acid or sodium chloride easily produces the blue color. Ostwald concludes that the blue color is due to the driving back of the dissociation of the cobalt chloride, the anhydrous salt being blue.

In a recent paper Donnan and Bassett[2] take the view that none of the theories thus far proposed is satisfactory. They make the suggestion that the blue color may be due to the presence of complex cobalt anions. They point out that the blue alcoholic solutions, when cooled down to —79°, become red, and conclude that this cannot be due to hydration. The question arises as to whether it may not be due to alcoholation.

The action of salts of zinc, mercury, cadmium, antimony and tin, in turning blue solutions of cobalt chloride red, is

[1] Grundlinien d. anorgan. Chem., p. 620.
[2] J. Chem. Soc., 81, 942 (1902).

explained as being due to the fact that these metals have a greater tendency to form complex negative ions than cobalt, and that they therefore break up the complex ions formed by the cobalt. This explanation seems decidedly forced. Evidence of a very direct kind should certainly be furnished that the above metals do have a very great tendency to form complex anions. In some of the above cases this is certainly not obvious.

Hartley[1] calls attention to some inaccuracies in the above paper. It is not at all certain that when hydrochloric acid is added to a solution of cobalt chloride the blue color is due to the same cause as when an aqueous solution is heated. Indeed, the absorption spectra in the two cases are quite different. Hartley points out, further, that the color of hot aqueous solutions was not supposed to be due to the anhydrous cobalt chloride, but to a dihydrate. Again, the spectra of a solution of cobalt chloride, saturated at 20°, and taken at the temperatures 23°, 33°, 43°, 53°, 73° and 93° are all different from the spectrum obtained from the anhydrous salt in absolute alcohol, and are also different from the cobalt chloride to which hydrochloric acid had been added.

Hartley also criticizes certain other points in the paper by Donnan and Bassett, but it would lead us too far to discuss these in detail.

Quite recently Lewis[2] has called attention to the importance of these color changes for the theory of hydrates in solution.

Jones and Bassett[3] have discussed the reactions described by Lewis, and Jones[4] has supplemented them by a number of other cases which bear directly upon the hydrate problem.

We shall now take up the work which we have carried out on the problem in hand.

APPARATUS.

The Spectrograph.—The apparatus was designed by one[5] of us in his previous study of the absorption spectra of the aniline

[1] J. Chem. Soc., **83**, 401 (1903).
[2] Z. physik. Chem., **32**, 222 (1905).
[3] THIS JOURNAL, **34**, 291 (1905).
[4] J. chim. Phys., **3**, 455 (1905).
[5] Uhler and Wood: Monograph, Carnegie Institution.

dyes. Since reference to earlier descriptions of the spectrograph may not be convenient, a brief account of its chief characteristics will be given below. The essential parts of a vertical section of the spectrograph are outlined in their exact relative proportions in Fig. 1., which is 1/15th of the natural size. This may be described as follows: In the first place each element of the system was adjustable in every respect. Light from a Nernst filament, N, was focused by the concave speculum mirror R, on the slit S, whence it continued to the grating G, from which a portion of it was disbursed in the direction of the sensitized film, F. The adjustable support of the mirror was rigidly attached to the main body of the spectrograph. The distances from the middle of the slit to the centres of the mirror and grating were, respectively, about 89.5 and 97.1 cm. The electrodes, E, were so located above the slit, as not to interfere with the passage of light from the reflector to the slit. No lenses or other reflectors were used. The micrometer head at M indicated the separation of the slit-jaws.

Q and Q′ denote a screen system, such that when Q was vertical the passage of light from the grating to the camera was not interfered with, whereas when Q was horizontal only ultra-violet light of shorter wave-lengths than 0.4 μ could reach the photographic film. PP is a horizontal platform with a scale along its front edge. By sliding horizontal opaque screens of various widths along this platform, it was possible to cut out completely any region or regions of wave lengths desired. In making certain tests the platform and sliding screens were very convenient. L is the section of a thin, black, metal shutter, capable of motion in a horizontal direction, and hence at right angles to the length of the photographic films or plates. In other words, parallel to the slit and to the rulings of the grating. A number of long, rectangular slots or openings, suitably spaced and proportioned, were present in this screen, so that strips of different widths of the films or plates could be exposed to the light from the grating, without causing any displacement of the sensitized surfaces with reference to the grating and slit. This was

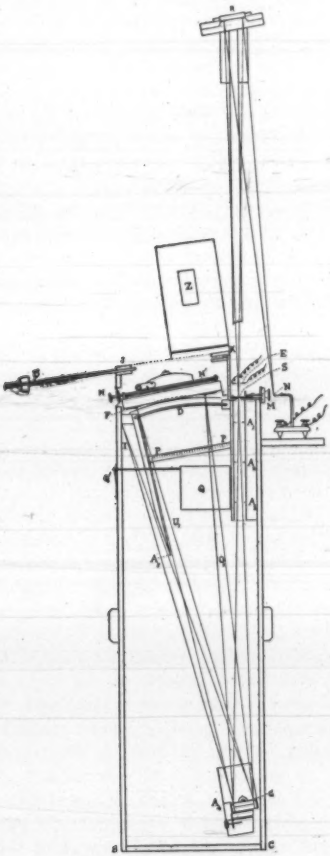


Fig. 1.

necessary for impressing comparison spectra, etc. H and H′ suggest the rack and pinion system, by the aid of which the films could have unexposed portions brought successively opposite to some selected opening in the slide screen L. D and D′ denote two of the four doors which gave access to the interior of the spectrograph, and which made it possible to close up the camera light-tight, while making various adjustments with the rest of the system. The camera was so made that when neither a film or plate was in position, it was possible for the experimenter to look directly at the grating and to make qualitative observations with the assistance of any eye-piece. Certain black-on-white scales and ruby glass windows (Z, for example) enabled the experimenter to know the precise relative positions of the various accessories in the interior of the spectrograph, when the entire system was shut up and exposures were being made. Numerous dull black diaphragms and screens (A_1, A_2, A_3, A_4, A_5, etc.,) protected the photographic film from the unusable light which came from the central image I, and from all the spectra except the one desired. U_1 and O_1 gave the extreme rays of so much of the first order spectrum as was studied photographically, that is, U_1 and O_1 correspond, respectively, to about 0.20 μ and 0.63 μ. The spectrograph was, of course, dull black both inside and out, and contained plaited black velvet wherever needed. A general idea of the size of this apparatus may be derived from the following dimensions. From R to the plane of BC = 198.5 cm.; BC = 34.5 cm.; the bottom edge perpendicular to BC = 27.5 cm.; BJ = 116 cm., and JK = 29 cm.

The Spectroscope.—This instrument was of the direct-reading type, and was obtained from Hilger of London. An orthagonal projection of this spectroscope on a horizontal plane is shown at H in Fig. II. Two details of the spectroscope deserve special mention. In the first place the instrument was so designed that when the prism was properly adjusted on its turn table, and the cross-hairs were correctly placed in the telescope, the wave length of any visible spectral line which appeared to be bisected by the point of intersection of the cross-hairs could be read off directly from the graduated

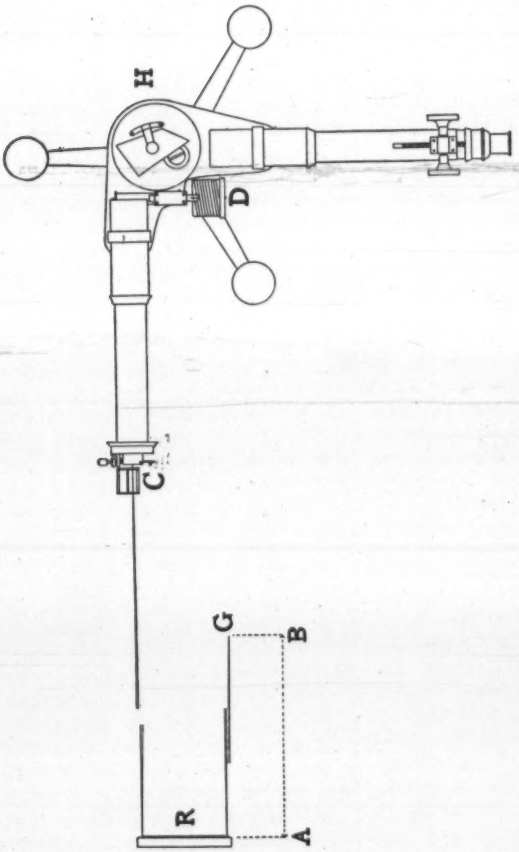


Fig. 2.

drum, D. In other words, all inconveniences attendant either upon the calibration of the spectroscope or upon subsequent references to a calibration curve, were avoided by the construction of the apparatus itself.

Secondly, all horizontal plane sections of the single glass prism were equal trapeziums; consequently, the beam of light, after entering the prism at the face nearest to the collimator, experienced one total interior reflection before it suffered final refraction out into the air opposite the telescope objective. This reflection diminished greatly the curvature

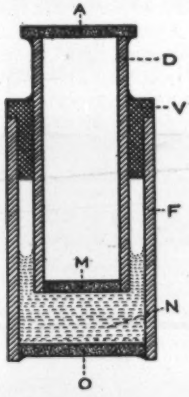


Fig. 3.

in the field of view of all spectral lines of which the light had not passed through the prism, at the angle of minimum deviation. Therefore, it was possible to use a greater length of slit and wider field of view than would have been justifiable with the usual type of triangular prism of equal dispersion. The chief practical advantage of the wide field of view was that two different spectra could be seen in this field, the one above the other, and readings could be taken directly from the graduated drum D, without any appreciable danger arising from curvature of spectral images.

The Cells.—For photographic purposes two cells were used in the study of aqueous solutions. One of these is shown in vertical section in Fig. 3. The diagram is of natural size. The cell was designed to fulfil 5 conditions: (i) to transmit, without sensible selective absorption, all radiations between wave lengths 0.80 μ and 0.20 μ; (ii) not to be acted upon chemically by the solutions placed in the cell; (iii) to cause the incident and emergent surfaces of the absorbing liquid to be plane and practically parallel; (iv) to be capable of adjustment with respect to the length of the column of liquid traversed by the light, and (v) to keep itself as clean as possible when in the immediate vicinity of the spark. The parts of the cell may be briefly described as follows. D and F were short sections of glass tubing, the ends of which were ground at right angles to their respective axes of revolution. A plane parallel plate of quartz M, was cemented in the lower end of tube D, and a similar quartz plate O, was cemented to the inside of the tube F, near the lower end of this tube. The position of the latter quartz plate relative to the end of the larger glass tube made it possible to slide the cell around on its lower end as much as desired, without scratching the under polished surface of the quartz, and without causing dust particles to adhere to it. It was necessary, of course, to use quartz in order to transmit the shorter ultra-violet waves. V shows a hard rubber cylinder, carefully turned in a lathe to fit neatly the outside of tube D. The collar or flange of this cylinder, when the cell was in adjustment, rested on the top of a larger glass tube in such a position as to establish parallelism between the quartz plates M and O. The smaller glass tube and the vulcanized ring were prevented from sliding along each other by a small amount of cement. It was very easy to scrape off this cement and to replace it subsequently, whenever it became necessary or desirable to alter the depth of the column of liquid between the lower quartz plates. The quartz plate A was an essential part of the cell. When it was not present, the passing of the spark between the electrodes above the cell produced violent disturbance in the column of air in the tube D, which resulted in the deposition on the quartz plate M of the decomposition

deposits of the electrode, *i. e.*, the oxides of cadmium, zinc, etc. Such a coating of foreign matter on the quartz, of course, could not be permitted. Care had to be taken to imprison dry air in the tube D when the plate A was cemented to the glass, because when this precaution was omitted a thin layer of moisture was deposited on the inner or opposing surfaces of the two quartz plates A and M, and produced spurious absorption effects on the spectrogram. After three of four photographic exposures with the spark had been made, the plate A invariably showed a thin whitish coating of the material, having boundaries which suggested a projection of the electrode on the quartz surface. This film was insoluble in water, and adhered very tenaciously to the polished quartz. It was easily removed, however, by rubbing with a piece of linen saturated with dilute hydrochloric acid. The coating was probably a mixture of the oxides of cadmium and zinc, driven hard against the quartz by the explosive violence of the spark. N shows the absorbing liquid in the cell. The light passed first through the quartz plate A, then through the dry air between A and M, then through the quartz plate M, next through the solution N, and finally through the quartz plate O. When the cell was filled with distilled water and extended as far as possible, no absorption, whether selective or general, could be detected photographically. Therefore, the selective absorption exhibited by the spectrograms was produced by the substance or substances in solution.

The cell just described was very well adapted to the study of plane parallel layers of liquid, having depths equal to and greater than 0.5 mm. On the contrary, its form did not lend itself as readily to the photographic study of extremely thin layers of very opaque solutions, as did that of another cell which had been designed by one of us[1] for an earlier investigation. A description of the cell last named may not be superfluous in this place. This piece of apparatus was used in the present work in such a manner as to impart to the absorbing liquid the form of a wedge or prism of zero thickness at the refracting edge. Consequently, the spectrograms obtained by

[1] Uhler and Wood: *Loc. cit.*

this cell in the path of the beam of light, exhibit, graphically, the variation which the limits of the regions of selective absorption experience when the depth of absorbing liquid varies linearly and continuously from zero to a few tenths of a millimeter at the greatest thickness.

The cell was made of 5 separable parts, as follows: (i) A brass framework upon which the other parts rested; (ii) a transparent tray without a lid, which confined the liquid in proper bounds; (iii) a transparent box-like system which gave the upper surface of the liquid the desired position; (iv) a vulcanized framework to hold the last-mentioned box in place; and (v) four mahogany pins or pegs to fasten the box to its framework.

(1) A side view of this work is presented in Fig. IV. This projection on a vertical plane is of natural size. There were

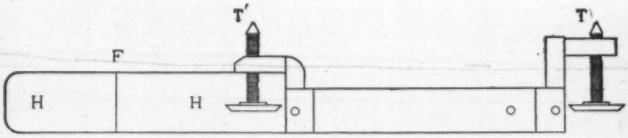


Fig. 4.

3 micrometer screws all of the same pitch, *viz.*, 1 turn = 1/48 in. = 0.053 cm. The heads of the screws are graduated on their upper surfaces in 10 equal parts. The screw T was in the immediate plane of the cell, while the remaining screws (T′ only is shown) were at the other end of the system, were equidistant from this plane, and as far apart as possible. The handle is denoted by HH. A black fiducial mark F, on a white ground, enabled the experimenter to tell what position the cell occupied with reference to the length of the slit of the spectrograph. The lower end of F moved over a scale parallel to the slit, and in the plane of the jaws of the latter.

The flange at the bottom of the framework was made of brass, only 0.014 cm. thick, so that the absorbing liquid might be as near the slit as possible.

(2) An accurately ground, plane parallel plate of quartz, 40 mm. long, 18.5 mm. wide and 2 mm. thick, had cemented

to the perifery 4 rectangular sheets of glass, 8 mm. high. Hence the greatest depth of liquid which could be studied by the aid of this cell was 6 mm.

(3) In Fig. 5, *a*, *b*, *c* and *d* designate the vertices of a section

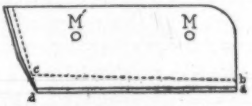


Fig. 5.

of the quartz plate, made by a plane perpendicular to the plane whose trace is the line *ad*. A*b* was 2 mm., *ad* was 34.8 mm., and the angle between the planes of *ad* and *bc* was 55 minutes of arc. The horizontal width of the wedge was 10 mm. Glass walls surrounded three sides of the wedge as the outline indicates. The reason for using the wedge was to counteract the deviation and dispersion produced by the solution in the cell. The angle of the liquid wedge could be varied until the deviation affected by the quartz wedge nullified the average action of the absorbing solution. At first it was supposed that with liquid wedges of 15 or 20 minutes of arc, a plane parallel quartz plate could be used successfully instead of the quartz wedge. Actual tests, however, showed that a plane parallel plate could not be relied upon, in general, to give correct results. Finally, the quartz wedge was made with the

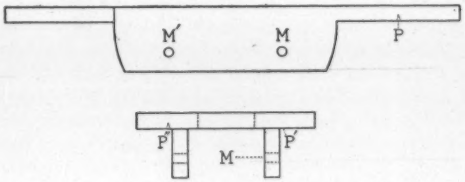


Fig. 6.

utmost care by an expert optician, special pains being taken to have the edge through D perpendicular to the plane, *a*, *b*, *c*, *d*, as sharply defined as possible, and the surface whose traces are noted by *ad* and *bc* were accurately plane.

Fig. 6 represents a side view and an end view of the vulcanite frame, into which the box just described fitted. This frame was shaped out of a single block of vulcanite, since experience showed that a cemented system of several pieces was not desirable; also a dielectric was needed to keep the sparks from jumping to the screws. P indicates a little depression which fitted over the point of the screw T. P′ designates the end of a straight line along which the rounded extremity of the screw T′ slid. P″ is the cross-section of a shallow, V-shaped groove along which the pointed end of the third screw T″ likewise slid. The perforations MM′, etc., correspond to each other, and to the associated wooden pegs mentioned above as (5).

Fig. 7 is an unconventional sketch of the cell when completely assembled.

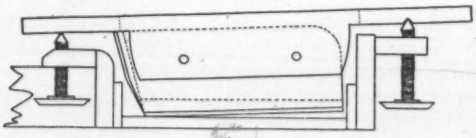


Fig. 7.

A cell of the construction just described is very well suited to the study of thin layers of solutions, in solvents of relatively high boiling points, such as water and amyl alcohol, but unless inclosed in some suitable vessel it is not applicable to solvents of lower boiling points, such as methyl alcohol, ether, chloroform, acetone, etc.

The cell used for making eye observations with the spectroscope, had to be constructed in such a way as to enable the observer to see simultaneously in the field of view of the telescope the absorption spectra of two solutions. This was necessitated by the very indefinite limits of absorption possessed by most of the regions and bands of absorption of the substances studied, *i. e.*, salts of cobalt and copper. In other words, it would have meant little or nothing to have attempted to observe one solution at a time, by setting the vertical cross-hairs at some definite wave length and to have given

the numerical value of this wave length as the limit of absorption or of transmission, since the gradation from complete transmission to total extinction was, in general, so very gradual as to make the setting just proposed practically impossible. Even if the cross-hairs had been set on a wave length for which it was estimated that the absorption was some definite fraction of complete extinction, this very act of estimation would have varied so greatly from one solution to the next as to cause the results to be imcomparable, and, hence, nearly worthless.

When, on the contrary, two absorption spectra are symmetrically placed in the field of view, it is easy to see at a glance all the qualitative differences between the two spectra, and, in addition, in many cases, to assign a number of the right order of magnitude to the relative displacements of the regions of absorption and of transmission in the superincumbent spectral bands.

Obviously, the light incident upon one of the solutions had to be of equal intensity to the light of the same wave length incident upon the other solution. Two modes of procedure at least could lead to this result. One scheme would be to use two equal, but entirely independent cells, place them symmetrically with respect to the source of light and the slit of the collimator, and to send two beams of light one through each cell, over equal optical paths (except the absorbing liquids) by means of two trains of reflectors or lenses suitably placed and adjusted. This plan was given a very thorough test, and was finally abandoned for the one explained below, for the reason that by the above-mentioned scheme it was necessarily troublesome to maintain two independent trains of reflectors or lenses, or totally reflecting prisms, which would produce in the field of view when the cells were removed, two emission spectra of exactly equal intensity and also close together.

A much simpler arrangement, and one which left nothing of a practical nature to be desired, was the following (*vide* Fig. 2): Light emitted by the Nernst glower G, fell upon the concave speculum reflector R. This reflector was the unruled

plate for a concave grating. The reflected beam came to a focus at the slit of the collimator, *i. e.*, the axis of the image of the glower coincided with that of the slit. Since the distance between *a* and *b* was 286.5 cm. and the distance between the reflector and the slit was 305 cm. (10 ft.) the beam of light did not greatly exceed the width of the glower's image for a distance of 3 or 4 cm. on both sides of the precise image. Consequently, when a cell of length less than 3 cm. and so constructed as to contain two solutions separated by a very thin diaphragm, was placed in contact with the slit jaws, any differences in the spectra of the light transmitted by the two liquids were correctly ascribed either to differences in absorption, or to inequalities in the transparency of the ends of the compartments of the compound cell. It was possible, of course, to make the halves of the cell so nearly alike as to produce no differential influence on the transmitted beams which could be detected visually. Even if this effective equality in the compartments of the cell could not have been realized, it would have been a comparatively simple matter to have interchanged the solutions in these compartments, and to have observed the phenomena which remained constant, and which were, therefore, due to the absorption of the liquids and not to the containing walls.

The more exact details and dimensions of the cell will now be given. The lower compartment was a box made of 5 rectangular strips of glass, cemented together. Its interior dimensions were, length 2.5 cm., width 2 cm. and depth 1 cm. The upper compartment was made of 4 vertical glass walls cemented together at the edges, and to a sheet of platinum foil as a bottom. The interior of this little box was, length 2.5 cm., width 0.94 cm. and depth 1 cm. The platinum foil was 0.06 mm. thick. Care was taken to make the 4 end pieces of glass of the same thickness, and from the same sheet. These ends were parallel to each other, and at right angles both to the bottoms and to the side walls of the respective compartments. Platinum was used as the partition between the boxes because it is opaque to visible radiations, and because it is not acted upon chemically by the solutions which

came in contact with it. The foil was selected as thin as was consistent with rigidity, so as to produce as narrow a band of separation between the two transmitted portions of the main incident beam as possible. With this same object in view, the least bit of cement was used to make the lower surfaces of the glass ends of the upper compartment adhere to the platinum. The two boxes were made separate and distinct, so as to facilitate washing, drying, etc. The lower compartment was made wider than the upper, so that when the latter was resting in position on top of the former, it was a simple matter to pour a given solution into the lower compartment until it came in contact with, and wetted the entire under surface of the platinum. Consequently, the liquids were as close together as the thickness of the platinum (0.061 mm.), and their spectra appeared sufficiently near in the field of view of the telescope to admit of accurate and easy comparisons.

A suitable stand for this apparatus was fitted with leveling screws, which enabled the experimenter to adjust the cell so that the plane of the platinum partition contained the axis of the incident beam, at the same time that the ends of the cell were perpendicular to this line.

Freezing Point Apparatus.—This system was of the improved Beckmann type, which can be found described in so many places that mere reference to it is quite sufficient here. The thermometer used with this apparatus was also of the Beckmann type. The smallest spaces on the stem of the thermometer signified 0°.02, and the total range of scale was 12°.

For temperatures lower than 10° or 11° below zero, 2 alcohol thermometers were employed. These instruments are graduated in 0°.5, and the lowest temperatures which they could register were, respectively, 55° and 82°.5 below the standard freezing-point of water.

With the Beckmann apparatus a mixture of ice, water and sodium chloride was used as the refrigerating agent. With the alcohol thermometers a suitable mixture of solid carbon dioxide and ethyl alcohol was employed.

Conductivity Apparatus.—The usual combination of a Wheatstone slide-bridge, with a small induction coil and telephone receiver, was used. The conductivity cell was of the U-tube pattern,[1] since most of the solutions were too concentrated to give sharp tone minima in cells of less ohmic resistance. All of the measurements for this system were made at 0°. Every necessary precaution was taken to obtain reliable data.

THE MAKING OF THE PHOTOGRAPHS.

Photographic Material.—Because of the short radius of curvature of the focal surface (about 49 cm.), celluloid films were employed in the majority of cases. The films used throughout were M. A. Seed's "L-ortho," cut, negative films, size 5 inches by 7 inches. The emulsion is by no means equally sensitive over the field of wave lengths studied photographically, *i. e.*, from 0.20 μ to 0.63 μ. The chief maximum of sensitiveness is in the yellow, at about 0.56 μ. A weaker maximum is near 0.49 μ. The middle of the less sensitive intervening region was very roughly 0.52 μ. For the short exposures given throughout, these films are not appreciably influenced by wave lengths longer than about 0.61 μ. Consequently, the dark regions extending from about 0.61 μ to the longer wave length end of such spectrograms as were obtained by the use of the Seed films, do not denote absence of light due to the absorption of some given solution, but they make manifest the lack of sensitiveness of the emulsion to the portion of the spectrum under consideration. The resultant effect of the Nernst glower and the Seed emulsion is best understood by referring to Plate I(*a*) for which the times for exposure were, in order, 2 seconds, 5 seconds, 15 seconds, 30 seconds, 1 minute, 2 minutes and 3 minutes. Various schemes to make the resultant action from the light of the Nernst glower and the Seed emulsion more uniform were tried, and other makes of films were tested, but no improvement on the simple combination of the source of light and emulsion just named was found. In fact, other photographic films did not act as well, on the whole, as those furnished by the Seed

[1] Jones and Getman: Z. phys. Chem., 49, 389 (1904).

Company. The films used were good in the ultra-violet, as is shown by the fact that with an exposure of 5 minutes the aluminium line at about 0.185 μ was clearly recorded, notwithstanding that the grating of the spectrograph was employed to disperse the light. When inspecting the photographs of absorption spectra, care must be taken to distinguish between possible spurious effects, arising from the maxima and minima of sensitiveness of the Seed films, on the one hand, and the phenomena of true absorption on the other. Observe the apparent band in the green as shown by Plate I(*a*).

As a check on the results obtained with the films, as well as to fill in the gap between about 0.59 μ and the nearer end of the field of view of the spectrograph, Cramer "Trichromatic" plates were used, since they were found to be the most satisfactory. The plates being plane and too rigid to be curved around into the focal surface of the grating had to occupy a mean position with respect to this surface. Since only a comparatively small region of wave lengths was recorded on the plates, no measurable errors were introduced. In fact, in the region considered, the second order ultra-violet of a discontinuous spectrum taken on a film and on a plate could be superposed line for line.

Sources of Light.—The sources of light and the selection of photographic material best suited for spectrographic work had previously been investigated by one[1] of us in an earlier research.

Nevertheless, a few words relative to these points may not be superfluous in this place.

For wave lengths from "above" 0.65 μ to "below" 0.326 μ, and for exposures of 2 minutes or less, the Nernst glower was found to be the most satisfactory. Prevailing circumstances made desirable the use of 106 volt glowers on a circuit carrying about 133 cycles. The emissivity of the Nernst lamp varies so very greatly with the electromotive force impressed upon its terminals, that it was obligatory to keep in series with the glower a Thomson A. C. ammeter, having a range from 0 to 2 amperes, and graduated directly to 0.02 ampere. Fluctua-

[1] Uhler and Wood: *Loc. cit.*

tions of more than 0.02 ampere invariably resulted in a spoiled photograph. Therefore, boxes containing variable metallic resistance were maintained in series with the ammeter, and thus, in spite of large changes of the load on the dynamo, due to other circuits, it was possible to prevent the effective current in the filament from changing by more than 0.01 ampere. The current was always 0.8 of an ampere. The ammeter was appreciably more sensitive to small changes in the terminal voltage than a comparably graduated Thomson A. C. voltmeter, because the current shunted through the voltmeter was not negligible in comparison with the current which fed the glower. Among other sources, the electric arc was given a fair trial and discarded, for two reasons. First, because of the intensity of the carbon and cyanogen bands; and second, because of the inconveniences resulting from its unsteadiness and great emission of heat.

For wave lengths between the strong ultra-violet of the Nernst glower and 0.20 μ a spark discharge in air of about 1 cm. in length was used. One electrode was composed of an alloy of equal parts by weight of cadmium and zinc, and the other was made of sheet brass. The alloy wore away so rapidly that the brass electrode was employed to diminish the mechanical labor attendant upon sparking the terminals. In order to produce a source of ultra-violet light which would have the same intensity from one end of the slit of the spectrograph to the other, for any one wave length, the electrodes were made in the shape of wedges or chisels, with the sharp edges parallel to the slit. The well-known distribution of a rapidly alternating current, necessitated curving the edges of the electrodes so that they were somewhat closer together at the middle than at the ends. Due to the tearing away of the metal and to various other causes, the innumerable thread-like sparks change the position of their ends so rapidly, that the integrating action of the photographic film recorded a perfectly uniform negative for exposure of 15 seconds or more. The electrodes had to be kept sharp and smooth, since when this was neglected, the elementary sparks persisted much longer in one position than in another and, consequently,

caused streaks of varying intensity to run along the negatives parallel to their length.

The current for the spark was obtained in the following manner: An alternating electromotive force of about 106 volts (133 cycles) was impressed on the terminals of an induction coil of unknown ratio of turns. Eight or nine amperes commonly flowed in the primary. The interrupter of the coil was thrown out of circuit, and the coil therefore performed the functions of a transformer. In parallel with the secondary was placed a Leyden jar about 18 inches high, and of unmeasured capacity. No auxiliary spark was introduced.

Exposures and Spectrograms.—When the complete spectrograms of a series of solutions were to be obtained, the succession of operations was, in general, as follows:

First, the depth of the cell for plane parallel layers of solution was made such that, judging from experience, and being guided by the depth of the color of the extreme solutions in their bottles, it would be neither too shallow to give appreciable absorption when the cell contained the most dilute solution, nor too deep to transmit enough light to affect the photographic plate when the liquid of deepest color was placed in the cell.

Second, a portion of each of the extreme solutions was successively poured into the cell which was, of course, clean and dry, and the corresponding spectrum observed by the aid of the spectrograph and a suitable eye-piece. In all cases, except those for which the solutions of deepest color were practically opaque to light for all depths greater than 0.5 mm., a depth of cell was soon found which enabled the absorption spectra of all the solutions of the series to be photographed on the same film, and with exposures of equal duration.

When 15 or 16 solutions belonged to one series, and this was often the case, the first 8 solutions were photographed on one-half of a complete 5 inches by 7 inches negative film, and then the remaining solutions had their absorption spectra photographically recorded on the other half of the same film. This break in the continuity of the work was due to the fact that the

capacity of the camera was limited to 8 spectral bands, each 6 mm. wide and spaced 0.05 mm. apart.

Except when there was some very good reasons for doing otherwise, care was taken to develop the halves of a film simultaneously, so as to subject all of the exposures to exactly the same chemical conditions. When the series of solutions comprised less than 15 members but more than 8, then the change from one-half of the film to the other was generally made as soon as the number of solutions which had already been photographed either equaled the number of those which remained or exceeded the latter number by unity. The reason for so doing is, doubtless, obvious. For any one solution the exposure with the Nernst glower was made first, the screen Q of the spectrograph being, of course, vertical. Then this screen was set horizontal, and the spark run for a definite length of time. Usually the light from the glower was caused to pass through the absorbing liquid for 1.5 minutes, while that from the spark for $1^1/_2$ minutes. These two intervals of time were so related that when no medium exhibiting appreciable absorption was in the path of the beams of light, the photographic impressions successively produced by the radiations from the Nernst glower and by the spark, blended into each other so well, that no discontinuity in the continuous background could be detected. The lengths of time of the exposures will be given only when they differ from 90 seconds and 80 seconds, respectively, for the glower and spark. The screen Q performed the function of protecting the negative film from contamination from the spectrum of the second order, which otherwise would have been superposed upon the spectrum of the first order.

As soon as the light transmitted by one solution had been recorded photographically, another solution was substituted for the preceding one, and also the film holder was moved along by the rack and pinion system through about 6.5 mm.; that is, until a strip of unexposed film came into the field of view of the grating. This strip was at a distance of a 0.5 mm. or so from the region previously exposed. After all of the 8 or less complete photographic strips on one-half film had

been exposed, the proper opening in the slide screen or shutter L [*vide* Fig. 1], was brought into position and the comparison spectrum impressed.

When spectrograms were made with trichromatic plates and the cell under consideration, the sequence of events was essentially the same as that just explained, except in so far as the exposure of the solutions to the light from the spark were omitted. Further, since plates of this kind are not as sensitive to orange and red light, as the Seed films are to most of the more refrangible colors, the time of exposure to the glower's radiations was usually 2 minutes.

Since the complete description of the manner of experimenting with the wedge-shaped cell has already been given elsewhere, and especially because a relatively small number of spectrograms were made with this cell in the present investigation, it seems desirable to discuss this matter only briefly here.

The length of the liquid wedge at right angles to its reflecting edge being about 3.5 cm. and the length of the spectrograph's slit being a little over 1 cm., the chief operation in manipulation of the wedge cell consisted in moving it over the slit jaws and parallel to the slit by proper amounts between successive exposures. Experience showed that the correct distance to move the cell was exactly 10.5 mm. The film holder had, of course, to be moved through corresponding distances between the respective exposures just mentioned. Consequently, the resulting spectrograms consist of 3 photographic impressions placed side by side and close together.

The edge of a spectrogram nearest to the comparison spectrum was produced by light which had passed through the thinnest layer of absorbing liquid, usually of zero depth; while the most remote edge resulted from the radiations transmitted by the deepest layer of solution. The slit width of the spectrograph was generally 0.08 mm.

Plates.—Before entering upon the presentation and discussion of the experimental results, a few words must be devoted to certain details which are common to most or all of the plates showing the absorption spectra of the solutions studied.

In the first place, when more than 8 strips belong to a plate, the corresponding photographic positives had to be made by placing the 2 half-negatives in the printing frame, with their edges as close together as possible, and with the line of the same wave length exactly opposite to one another, *i. e.*, in proper register. In general, the line of contact of the 2 half-films shows in the figures as a streak of intensity different from that of the adjacent portions of the print, and extending from one end of the figure to the other. It is more than likely that slight errors in wave length have been introduced in some cases by this process of reproduction, which, however, was necessitated by the limited capacity of the film holder. In most cases these errors can be fully allowed for, by observing the relative displacement of the two segments of some chosen sharp emission line, which appear on the two photographic strips lying on both sides of, and closest to the above-mentioned streak. Whenever this line of demarkation does not show distinctly on the figure, a definite statement will be made in the text as to where the change from one half-film to the other is. However, in cases when no emission lines are present on the two strips bordering on the streak, the reader has no very good means of telling whether the half-films were in exact register or not, and, therefore, he will have to assume that no appreciable error has been introduced in this manner. Moreover, shifts in wave lengths due to the motion of the film holder and its guides or ways, are present in most of the figures. These displacements can be measured and allowed for in the manner suggested above. It must be borne in mind that the solutions studied, present such washed out limits to most of their regions of absorption, that it is not possible to assign numbers to the wave lengths of these boundaries, which would be nearly as accurate as the determination of the relative shifts of the parallel photographic strips. Moreover, with bands of absorption of the type just referred to, their apparent ends would be displaced in wave length by various experimental causes, such as variations in the intensity of incident light, changes in the time of exposure to the radiations, changes in the duration of development,

variations in the temperature and composition of the developer, etc. The best that could be hoped for was to obtain parallel spectrographic strips of the solutions of a given series, which exhibit the spectral changes caused by the solutions themselves, and only by the solutions, extreme care being taken to keep all other conditions as nearly constant as possible. The figures, therefore, show the relative changes in the absorption spectra of the solutions of one set with accuracy. Whenever there was the slightest possibility of spurious results arising from the chief maxima and minima of sensibility of the Seed emulsion, the results were checked by taking additional plates with the Cramer trichromatic emulsion, which has not the same sensibility curve as the Seed film. In all cases the series of eye observations with the spectroscope, not only supplement the photographic data in the red, but they also serve as an additional qualitative check on the entire visible region.

For comparatively accurate estimations of wave lengths, one comparison spectrum of the emission lines of the spark has been reproduced in each photographic figure. The most intense and sharpest lines have been numbered in Plate I(*a*). This plate serves as a key to the table of wave lengths given in a later paragraph.[1]

Since the spark lines of cadmium, zinc, oxygen and nitrogen are not equally spaced, the comparison spectrum mentioned above, together with its key and table, is very inconvenient for most purposes of reference. Consequently, a numbered linear scale of wave lengths has been printed by the side of each complete spectrogram. Although it is not professed that these scales are as accurate as they are suggestive and convenient, nevertheless, it is only fair to call attention briefly to the chief errors possessed by them. As is well-known, a concave grating gives spectra which depart more and more from normality, as we recede from the principal axis of the reflector on which the lines of the grating are ruled. Therefore, a strictly linear scale cannot correctly register all the wave lengths of a grating spectrum. Nevertheless, the grating

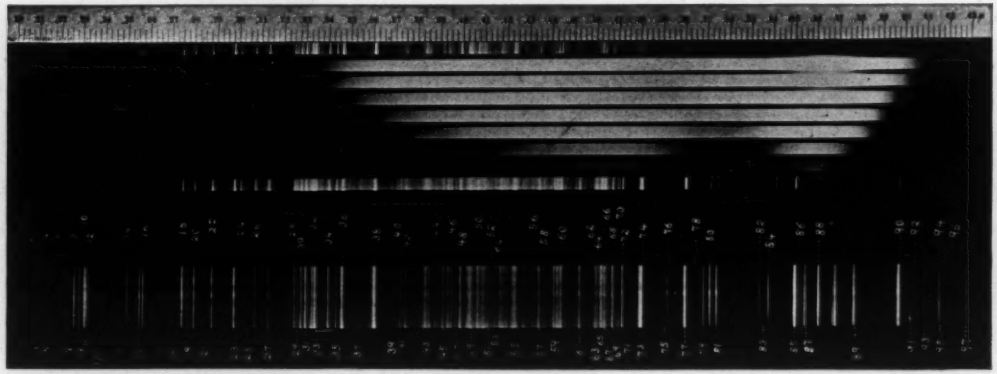
[1] Uhler and Wood: *Loc. cit.*

belonging to the spectrograph was of such short focus that for the region of wave lengths of the first order spectrum used, the error just mentioned was negligible in comparison with those explained below.

It is a well-known fact that celluloid negative films, after development, fixing and drying, differ appreciably in length from the same linear dimension which they possessed before being so treated. If all the films of one make would behave quantitatively in exactly the same way, the variations in length to which attention has just been called, would be of no importance from the present point of view. But films of the same kind change by very different amounts, and this phenomenon is inconvenient, to say the least. Therefore, to have linear scales to fit accurately each and every one of the complete spectrograms, it would be necessary to make as many different scales as there are different distances between the extreme spectral lines, say, throughout the entire series of spectrograms. Obviously, to do this would entail an amount of labor which would be utterly disproportionate to the gain in accuracy finally obtained. Consequently, only 4 or 5 negative scales of different total length were obtained by photographic production from the same paper scale, which was ruled and numbered for the present work. Since the negative scales cover the entire range of variation in length of the spectrograms, the wave lengths of selected lines, when read off from the scales on the published plates, ought not to contain any large error.

In making the positives the scale line numbered 48 was placed opposite to the corresponding strong emission line of the comparison spectrum. The latter line has a wave length of about 4800.1 Ångström units, and is designated by 73 on Plate I(*b*). It is probable that in a few cases the two lines just named, the one on the negative scale and the other on the negative spectrogram, were displaced a little with respect to each other in the process of printing.

To avoid having the lines of the numbered scale too close together, each of the smallest intervals denotes 25 Ångström units.



Plates I(a) and I(b).

The wave lengths of the numbered lines of Plate I(*b*)[1] were derived from the two following sources:

"An Introduction to the Study of Spectrum Analysis," by W. M. Watts.

"Measurements of the Wave Lengths of Lines of High Refrangibility in the Spectra of Elementary Substances," Hartly and Adeney. From the *Philosophical Transactions* of the Royal Society, Part I, 1884.

1.	2024.2 Zn.	32.	3329.3 Air.
2.	2060.8 Zn.		3331.5 Air.
	2062.8 Zn.	33.	3345.1 Zn.
3.	2099.0 Zn.		3345.5 Zn.
4.	2138.3 Zn.	34.	3403.7 Cd.
5.	2144.5 Cd.	35.	3436.9 Air.
6.	2194.7 Cd.	36.	3466.3 Cd.
7.	2239.9 Cd.		3467.8 Cd.
8.	2265.1 Cd.	37.	3535.0 Cd.
9.	2288.1 Cd.	38.	3610.7 Cd.
10.	2306.7 Cd.		3613.0 Cd.
11.	2313.0 Cd.	39.	3682.6 ?
12.	2321.2 Cd.	40.	3712.2 Air.
13.	2329.3 Cd.	41.	3726.6 Air.
14.	2502.1 Zn.	42.	3749.8 Air.
15.	2558.0 Zn.	43.	3839.3 Air.
16.	2573.1 Cd.		3841.7 Air.
17.	2710.1 Air.	44.	3881.9 Air.
	2712.6 Zn.	45.	3919.2 Air.
18.	2748.7 Cd.	46.	3954.8 Air.
19.	2770.9 Zn.		3956.2 Air.
20.	2801.0 Zn.	47.	3972.5 Air.
21.	2837.0 Cd.	48.	3995.1 Air.
22.	2880.9 Cd.	49.	4041.4 Air.
23.	2980.8 Cd.	50.	4070.0 Air.
24.	3007.0 Air.		4072.4 Air.
25.	3035.9 Zn.		4076.1 Air.
26.	3072.2 Zn.	51.	4119.4 Air.
	3076.0 Zn.	52.	4132.8 Air.
27.	3133.3 Cd.		4133.8 Air.
28.	3250.5 Cd.	53.	4145.9 Air.
29.	3261.2 Cd.	54.	4151.9 Air.
30.	3282.4 Zn.		4153.6 Air.
31.	3302.7 Zn.		

[1] The negative was not a single exposure. To stand reproduction the extreme ultra-violet was "favored."

55. 4228.5 Air. 4236.7 Air. 4241.9 Air.
56. 4316.2 Air. 4318.7 Air.
57. 4349.5 Air.
58. 4367.9 Air.
59. 4415.1 Air.
60. 4447.1 Air. 4447.2 Air.
61. 4530.1 Air.
62. 4576.2 Cd. 9_2.[1]
63. 4601.6 Air.
64. 4607.3 Air.
65. 4614.0 Air.
66. 4621.6 Air.
67. 4626.0 Cd. 11_2.
68. 4630.7 Air.
69. 4641.9 Air. 4643.4 Air.
70. 4649.2 Air.
71. 4680.4 Zn.
72. 4722.3 Zn.
73. 4800.1 Cd.
74. 4810.7 Zn.
75. 4912.3 Zn.
76. 4924.8 Zn.
77. 5002.7 Air. 5005.7 Air.
78. 5045.7 Air.
79. 5086.1 Cd.
80. 5116.0 Zn. 15_2.
81. 5146.2 Cd. 16_2.
82. 5338.6 Cd.
83. 5354.4 Cd. $—_2$.
84. 5379.3 Cd.
85. 5497.4 Cd. 18_2.
86. 5509.0 Zn. $—_2$.
87. 5541.8 Zn. 19_2.
88. 5602.0 Zn. 20_2.
89. 5761.8 Cd. 22_2.
90. 5961.6 Cd. 23_2.
91. 6014.0 Air 24_2.
92. 6035.0 Zn. $—_2$.
93. 6071.8 Zn. 25_2.
94. 6144.4 Zn. 26_2.
95. 6152.0 Zn. 26_2.
96. 6160.4 Cd. $—_2$.
97. 6266.6 Cd. 27_2.

EXPERIMENTAL FACTS AND DATA.

In the succeeding pages the experimental material will be presented in the following order: All the facts obtained by spectrographic means, pertaining to the simple aqueous solutions containing cobalt chloride will be given first; then those relating to cupric chloride, and, finally, those pertaining to cupric bromide. Following this, the solutions obtained by adding calcium chloride, calcium bromide, or aluminium chloride, to the simple aqueous solutions, will be taken up in the order in which the dehydrating agents have been named. For any set of solutions, the data obtained by the photographic method will appear immediately after the record of the concentrations. The results of eye observations with the spectroscope will then be presented, and, following this, the freezing point lowering will be given. Conductivity

[1] Subscripts 2 denote the second order.

data expressed in reciprocal ohms and reciprocal centimeters will then be presented and, finally, attention will be called to any other facts which have been noted.

Solutions.—The aqueous solutions investigated are made up as follows: A chosen volume of the mother solution of a colored salt was measured out from a burette, into a measuring flask of known capacity. The portion of solution in the flask was then diluted by the addition of pure water which had been distilled several times, so that its conductivity was as low as 1.1×10^{-7} at 0° on the average, until the volume of the resulting homogeneous liquid was exactly equal to the fixed capacity of the flask. The same flask was used in making up all the solutions studied throughout the entire investigation. The concentrations will always be expressed as multiples of normal. The term "normal" will be used exclusively to mean gram-molecular normal; *i. e.*, a liter of solution which contains just as many grams of anhydrous salt as there are units in the number expressing the molecular weight of the salt, is defined as "normal." Hence, if a liquid is composed of n gram-molecules of salt in a liter of solution, its concentration is n times normal; n can have any positive value, integral or fractional. In general, several solutions of one set were made up with reference to their colors; in other words, in such a manner as to employ as wide a range of concentrations as could be conveniently photographed, and at the same time to bring out the delicate changes in tint by having the successive differences in concentration as small as desirable.

When a solution contained both a colored salt and a colorless dehydrating agent, it was prepared as follows: A certain known volume of the mother solution of the colored salt was measured out into the flask mentioned above. Then a definite volume of the mother solution of the dehydrating agent was poured into the flask containing the colored liquid. The sum of the 2 volumes just specified was less than the fixed capacity of the flask. In special cases shrinkage in volume on mixing would make this statement slightly inexact. Finally, the mixture of the mother solutions was made up to the full volume of the measuring flask by the addition of

pure water. In a series of solutions containing the same pair of salts two things were kept constant. First, the mass of colored salt present, and second, the total volume of the solution. The chief variable was the mass of dehydrating agent in the several solutions. As formerly, the color changes were the criteria governing the number and respective concentrations of the solutions of any one series. It was not deemed necessary to determine the specific gravities of the liquids studied. The details relating to the individual salts will now be considered.

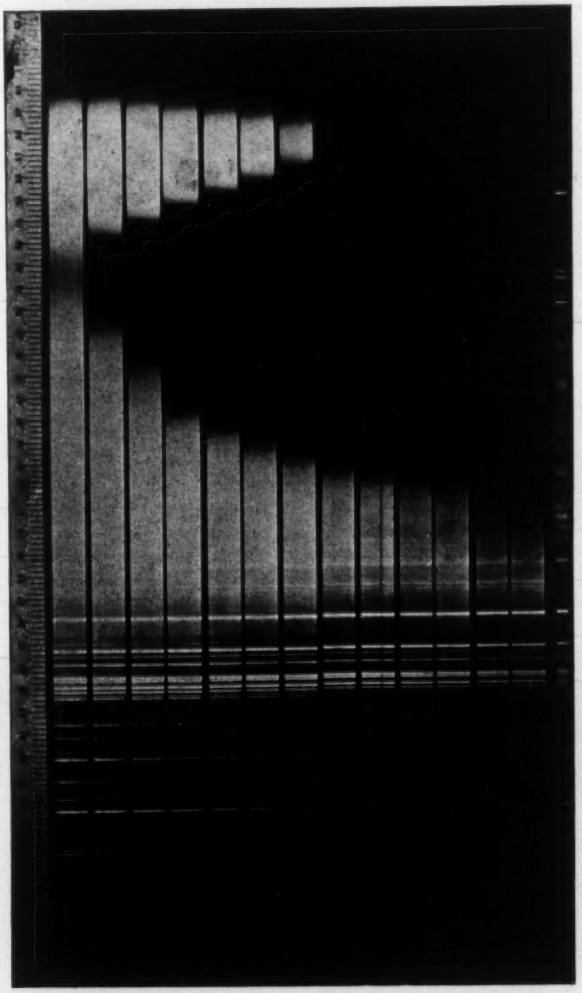
Cobalt Chloride.—(See Plates II., III(*a*), which has been reduced to seven-eighths of its original size, and IV(*a*).) The concentrations of the solutions were 0.217, 0.379, 0.542, 0.759, 0.976, 1.192, 1.409, 1.626, 1.843, 2.060, 2.276, 2.493 and 2.710. Therefore, the first 2 increments of concentration were each equal to 0.1626 and each of the remaining successive differences equal to 0.2168.

The number 2.710 belongs to the mother solution of cobalt chloride. The color of the liquids increased in depth from a delicate pink or rose color to a very dark red. In layers of more than about 1 cc. in thickness, the more concentrated solutions were opaque to ordinary light. The solution whose concentration was 0.217 N, gave the absorption spectrum shown by the photographic strip nearest to the numbered scale of Plate II. The next strip corresponds to the concentration 0.379, etc., across the spectrogram. Thus, the strip nearest to the comparison spectrum is associated with the mother solution. The common depth of the absorbing layers of liquid was 0.67 cm. The spectrogram shows 2 regions of absorption, the one in the remote ultra-violet and the other in the blue and green.

The most dilute solution transmitted the line at 2138.3, but nothing of shorter wave length. All numerical data were derived from the negatives and not from the plates.

The background stops at about 2265. The most concentrated solution barely transmitted the line of wave length 2502.1, and cut out practically all the continuous background which is more refrangible than 2748, due regard being had for

Plate II.



the successive increments of concentration of the solution. For the most dilute solution, the maximum of absorption in the green was at about 0.515 μ. The general contour of the limits of ultra-violet transmission can best be understood by referring to Plate II.

The region of absorption encroached on the shorter wave lengths, more rapidly than on the longer ones. The asymmetry of the region may be due to the superposition of 2 close, unresolved bands, of which the more refrangible was the weaker. For the seventh solution of concentration 1.409, the middle of the photographic region for absorption was at 0.503 μ. The more refrangible end of this band was at about 0.432 μ for the more concentrated solution.

The absorption spectra of the 5 most concentrated solutions were photographed with a red sensitive plate, and the result is reproduced as Plate III(*a*). The depth of cell was 0.67 cm., as before, but the exposure with the Nernst filament was 2 minutes in length. The photographic limits of absorption of the solution of concentration 1.843 were about 0.438 μ and 0.565 μ, while those for the mother solution were about 0.427 μ and 0.585 μ. The apparent displacement of the middle of the band from 0.502 μ to 0.506 μ, with increasing concentration, is probably due, in part, to weak photographic action in the neighborhood of the less refrangible end of the absorption band of the most concentrated solution. Moreover, the negative plate was undeveloped.

Plate IV(*a*) shows the continuous variation of thickness of the absorption of the mother solution of cobalt chloride. The solution was placed in the wedge cell and consequently the depth varied linearly. To bring out the band in the blue-green, zero depth of absorbing layer could not be used. The least and greatest depths of liquid were 0.53 mm. and 1.09 mm., respectively, and the angle of the cell was 58′.5. As usual, the side of the spectrogram corresponding to the least depth of the liquid lies nearest to the comparison spectrum. The times of exposure for the glower and spark were 90 seconds and 80 seconds, respectively. The band in the blue-green has its centre about 0.520 μ. It seems to be slightly

asymmetric, but this appearance is doubtless exaggerated by the great sensitiveness of the Seed film to yellow light. The end of the band in the extreme ultra-violet varies slightly with increasing thickness of the absorbing layer. Faint transmission begins about 0.245 μ. A negative taken with the cell set at an angle of 35′.1, and commencing at zero depth showed practically no band in the green, but it did show a definite curved line of absorption in the remote ultra-violet. A general idea of the course of this curve can probably be gathered from the following statements: The least trace of the zinc doublet at 2062 A. U. was shown at the very edge of the negative. The spectral lines of wave length 2144.5 and 2194.7 jutted out from the edge of the spectrogram, through distances of, approximately, 6 and 9 mm. The continuous background ended at 0.238 μ on the edge of the negative corresponding to the greatest depth of solution in the wedge.

Eye observations with the spectroscope showed the facts recorded below. The depth of the cell was the same as when photographic exposures were being made. For the solution of concentration 0.217, the spectrum began at about 0.775μ. No bands were visible in the red. The band in the blue-green was very faint and diffuse.

The solution of concentration 0.759 also showed no band in the red. The most intense absorption seemed to be at 0.525 μ, but the blue-violet side of the region was so much more diffuse than the yellow side, that not much importance should be attached to this number. Due allowance has been made for the fact that with a simple prism the dispersion increases as the wave length decreases. However, the spectroscopic observations confirm qualitatively the spectrographic results.

No bands could be seen in the red for the solution of concentration 1.409, and absorption was complete from about 0.558 μ to about 0.450 μ.

The violet was greatly dimmed.

Similarly, the solution of concentration 2.060 exhibited no bands in the red. The band in the midst of the visible region extended from 0.571 μ to, roughly, 0.488 μ. As previously,

Plate III(a). Plate III(b). Plate III(c).

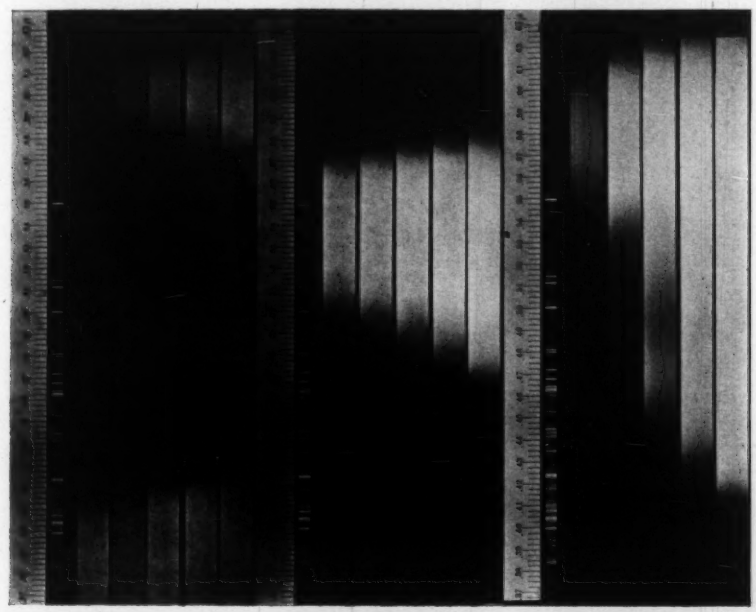
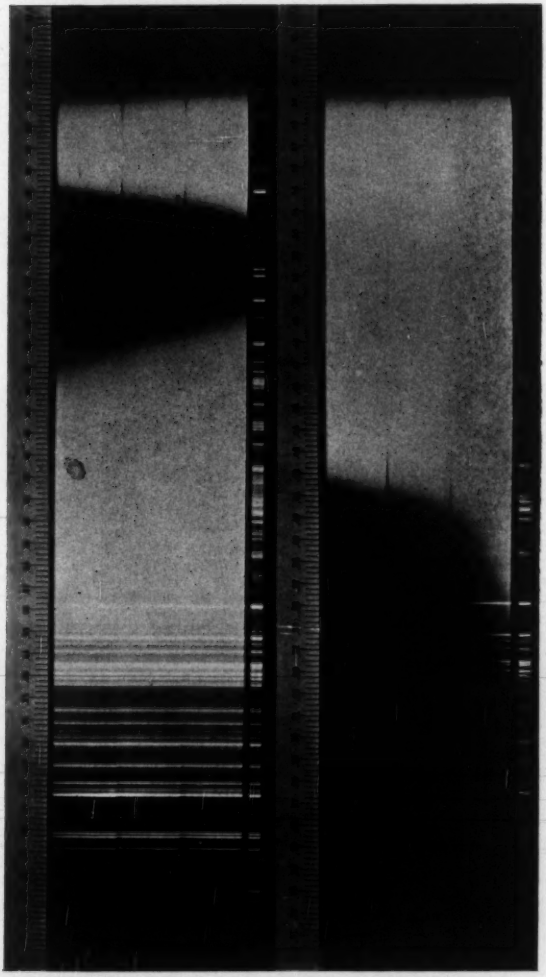


Plate IV(a).

Plate IV(b).



the end of the band nearer the yellow was much more definite than the end in the indigo. The violet was rather faintly transmitted.

The mother solution showed a series of weak bands in the red. Only the orange and certain parts of the red were transmitted, and the light was considerably weakened even in these regions. It would seem, at first sight, that the last statement is inconsistent with the wave length 0.432 μ, which the spectrogram gives as the extreme, least refrangible boundary of the region of transmission in the ultra-violet and violet, when the well-known fact that the average normal eye is sensitive to waves at least as short as 0.400 μ is taken into account. The apparent discrepancy is easily accounted for by the following considerations. The photographic film exerted an integrating action over a period of 90 seconds, whereas the retina does not add up successive stimuli of the same spot for nearly so long a time. Moreover, the dispersion of the spectroscope in the violet was much greater and the spectrum no brighter than that of the grating in the same region. The spectrum began about 0.773 μ. From this point the intensity of transmission rose gradually to a maximum, and then decreased to a faint minimum at 0.714 μ. This faint absorption band was followed by another one at 0.676 μ. The spot of maximum brightness between these bands was at about 0.669 μ. Between 0.67 μ and 0.59 μ the incident light had suffered less general absorption than anywhere else in the visible spectrum, with the exception that a faint, narrow absorption band was just noticeable at 0.636 μ. Transmission ceased at about 0.588 μ.

Cupric Chloride.—(See Plates III(*b*), IV(*b*), and V., which last has been reduced to three-fourths of its original size.) The concentrations of the solutions were 0.239, 0.318, 0.557, 0.795, 1.113, 1.272, 1.431, 1.590, 1.749, 2.067, 2.385, 2.073, 3.021, 3.339, 3.657 and 3.976. The successive differences in concentration were 0.079, 0.239, 0.239, 0.318, 0.159, 0.159, 0.159, 0.159, for the first 9 solutions, and 0.318 for all the rest. The last number belongs to the mother solution of copper chloride.

The color or the most dilute solution was a delicate blue, then, as the concentration increased, the color of the solutions passed through various shades of greenish blue or bluish green, of light green and, finally, the mother solution was a deep, dark green.

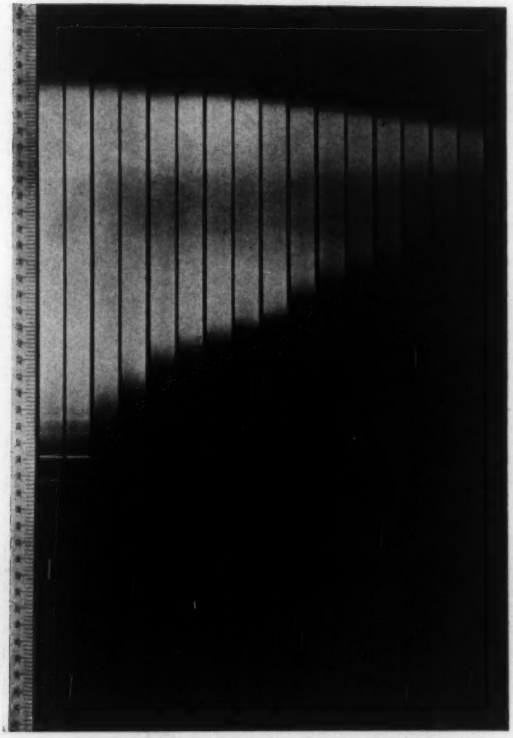
Plate V. will be considered first. The solution whose concentration was 0.239 N has its absorption spectrum shown by the photographic strip nearest to the numbered scale. The remaining strips succeed one another in the order of increasing concentration, so that the strip nearest to the comparison spectrum corresponds to the mother solution. The effective depth of the cell was 0.67 cm.

The spectrogram shows 2 regions of absorption, the one in the ultra-violet, violet-blue, etc., and the other in the orange. Absorption in the region last named is to be inferred from the fact that the ends of the photographic strips corresponding to the more concentrated solutions do not lie in a straight line at right angles to the length of the spectrogram, but they recede from the end of the plate as the concentrations increase.

If there has been no strong selective absorption in the yellow-orange, then all the photographic strips would have faded out at the same distance from the end of the plate, due simply to the lack of sensitivity of the Seed negative films to light of relatively small refrangibility. The most dilute solution transmitted a faint trace of the spark line at 3250.5, but nothing of shorter wave length. The absorption of solution of concentration 0.318 was very little more extended than that of the most dilute member of the series.

This is due to the fact that these 2 solutions did not differ greatly in concentration. To obtain the clearest view of the variation of absorption with concentration, it is best to fix the attention only upon those photographic strips that correspond to the solutions whose concentration differed by the same amount, *e. g.*, by 0.318. In other words, omit the first, second, third, sixth and eighth strips from consideration for a moment. It is then seen that a smooth curve is presented by the limits of the region which absorbs all of the shortest

Plate V.



waves of light. Also the successive increments of absorption become less and less, as the concentrations of the solutions increase. For example, the seventh photographic strip ends about 200 A. U. farther along than the fifth strip. The twelfth, 90 units beyond the eleventh, and the sixteenth 55 units beyond the fifteenth. The region of transmission for the mother solution extended from about 0.483 μ to 0.574 μ.

The negative for Plate III(*b*) was obtained with a Cramer "Trichromatic" plate. The exposure for each of the 5 most concentrated solutions was 2 minutes in length. The depth of the cell was 0.67 cm., as before. This spectrogram shows correctly the limits of transmission not only at the blue side, but also towards the red, since the photographic plates would have been made deep black as far as its very ends, if the light had not passed through the absorbing layer of liquid. The limits of the region of transmission for the solution whose concentration was 2.073, were 0.460 μ and 0.593 μ, while the corresponding numbers for the mother solution were 0.485 μ and 0.583 μ. Therefore, the rate of increase for absorption is greater at the more refrangible end of this region than at the less refrangible end. In fact, the middle of the transparent region shifted towards the red by about 75 A. U. as the concentration increased from 2.073 to 3.976.

Plate IV(*b*) was obtained with the wedge-cell set at an angle of 19′.5 and starting with nearly zero depth. The thinest layer transmitted a trace of the cadmium line at 3133.3. The boundary of the ultra-violet region of absorption then curved around as shown by Plate IV(*b*), and reached about 0.400 μ, corresponding to the thickest part of the wedge. The great intensity of the ultra-violet absorption is worthy of note.

Eye observations fully confirm the results obtained by the photographic method. For the most dilute solution, transmission began at about 0.727 μ, *i. e.*, in the bright red. As more and more concentrated solutions were observed, the absorption at the red end of the spectrum extended gradually to shorter and shorter wave lengths. The following numbers were recorded as the wave lengths of the extreme limits of visual transmission for the first, fourth, seventh, tenth, twelfth,

fourteenth and sixteenth solutions, named in the order of increasing concentration, *viz.*, 0.727 μ, 0.677 μ, 0.646μ, 0.634 μ, 0.624 μ, 0.616 μ, and 0.660 μ, respectively. Reasons why the eye observations agree qualitatively, but not quantitatively, with the photographic results are too simple to need explanation. The limits of the more refrangible ends of the regions of transmission of the solutions, as obtained with the spectroscope, are not as satisfactory as the results obtained photographically, because the absorption fades away very gradually in the part of the spectrum under consideration. Therefore, no more wave lengths will be given for the simple solutions of copper chloride in water.

Cupric Bromide.—(See Plates III(*c*), VI. and VII(*b*).) The last two are reduced to three-fourths of the original size. The concentrations of the solutions photographed were 0.175, 0.350, 0.394, 0.437, 0.481, 0.525, 0.568, 0.612, 0.656, 0.700, 0.874, 1.049, 1.224, 1.399 and 1.574. The first, second, sixth and tenth solutions, as well as those having greater concentrations than the tenth, form a series in which the successive concentrations differ by the same amount, namely, by 0.175. The remaining solutions were interpolated in the series just mentioned, and the successive increments of concentration thus produced are all equal to 0.044, *i. e.*, to one-quarter of the greater common difference, 0.175. In this case the concentration of the mother solution was 2.186. The solutions, when in the plane parallel cell, which was adjusted at a depth of 2 mm., varied from almost no color for the most dilute solution, through different shades of clear green and yellowish-green, to a very dull brownish-green for the solution of concentration 1.574. In the bottles, of course, the colors were much deeper than in the cell, and the more concentrated solutions of the set photographed, together with the mother solution, were apparently opaque to light.

In Plate IV., as usual, the photographic strips showed the absorption spectra of the solutions of concentration 0.175 and 1.574 are adjacent, respectively, to the numbered scale and to the comparison spectrum. The 15 strips succeed one another in the order of increasing concentration. The

most dilute solution transmitted an extremely faint trace of the line at 3250.5, but nothing of shorter wave length. Due regard being had for the successive difference in concentration, it is seen from the spectrogram that the region of absorption which includes the ultra-violet increases in a perfectly regular way for about the first 12 solutions. The thirteenth strip begins to show weak absorption at about 0.517 μ and the fourteenth brings out the presence of this band very noticeably. The long, prenumbra-like region, which extends from about 0.45 μ to 0.53 μ on the fourteenth strip, is entirely absent from the fifteenth. The shortest wave length recorded by the spectrogram for the most concentrated solution is, approximately, 0.543 μ. The last 3 or 4 photographic strips, which correspond to the more concentrated solutions, indicate the presence of a region of weak general absorption in the orange and red. In drawing conclusions from spectrograms of solutions of copper bromide, care must be taken to avoid errors which might arise from the maxima and minima of sensitivity of the photographic emulsions, especially when Seed orthochromatic films are involved [*vide* Plate I(*a*)].

The statements made above are substantiated for the 5 most concentrated solutions by Plate III(*c*), the negative for which was a "Trichromatic" Cramer plate. The cell was adjusted to a depth of 2 mm. as before, and the length of each exposure to the light from the Nernst glower was 2 minutes. That the absorption in the orange-red is weak, in general, is shown by the fact that 4 of the 5 photographic strips of the negatives were blackened to a greater or less degree, as far as the end of the field of view of the camera, while the fifth strip was very faint at this limit.

On Plate III(*c*), the prenumbra mentioned above is clearly shown by the third and fourth strips, coming from the sides of the spectrogram adjacent to the numbered scale. Also the fifth strip shows no sign of this region of weak transmission, as was also the case with the fifteenth strip in Plate VI. The shortest wave length recorded on the negative Plate III(*c*), for the most concentrated solution, was 0.541 μ.

The dependence of the limits of absorption upon thickness of layer for the mother solution of copper bromide was shown graphically by Plate VII(*b*). The angle of the wedge-cell was 27′.3 and the depth of solution varied linearly from about 0 to 0.25 mm. In the deeper portions of the cell the solution appeared dull brown. The washed-out band in the blue-green was observed with the eye-piece and, consequently, its presence on the spectrogram is not due to the photographic film alone. As for the chloride of copper, so also for the bromide, the absorption of the ultra-violet is very strong. The shortest wave length recorded on the negative for the least depth of liquid is 3250.5 A. U., and that for the greatest depth is about 0.438 μ; Plate VII(*b*), shows the boundary of the ultra-violet band sufficiently well to make further comment on this region superfluous. The band in the green has its middle at, roughly, 0.518 μ. The fact that the ends of the photographic strips resulting from the 3 successive exposures, which ends are in the vicinity of 0.597 μ, suggest a straight line which slants with respect to the length of the spectrogram, calls attention to the general absorption of the least refrangible portions of the spectrum.

The following facts were obtained by eye observations with the spectroscope, the cell having the same depth as above. The numbers recorded for the limits of transmission in the red for the first, third, fifth, seventh, ninth, eleventh, thirteenth and fifteenth solutions, named in the order of increasing concentration, were 0.750 μ, 0.730 μ, 0.725 μ, 0.720 μ, 0.712 μ, 0.707 μ, 0.690 μ, 0.680 μ, respectively. Since the band in the red has a diffuse end in the visible spectrum, the data just given are useful only in so far as they indicate roughly the progressive increase of absorption with the like variation in concentration, but they are not to be considered as very accurate. The wave lengths of the limits of absorption of the band which extends from the ultra-violet into the visible spectrum, as obtained for the solutions mentioned in the above list, agree qualitatively with those derived from the spectrograms; and since the former are less reliable than the latter, they will not be given here. Special attention, however, was

Plate VI.

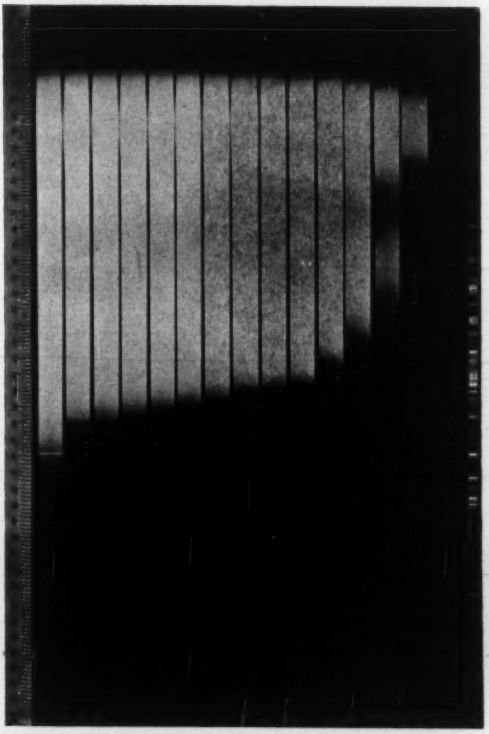


Plate VII (a).

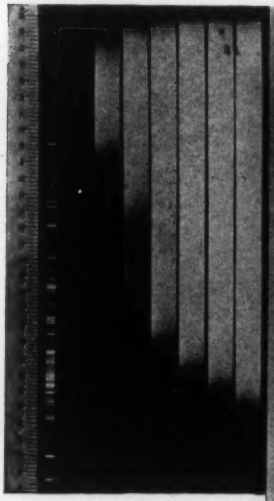
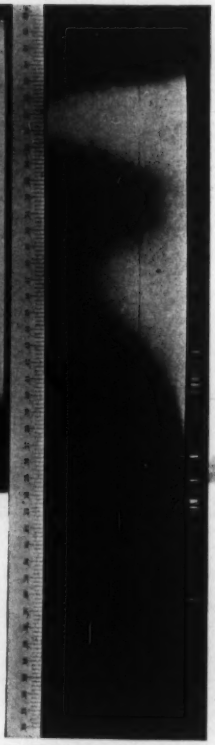


Plate VII (b).



directed to the solutions of concentration 1.224 and 1.574, in order to find out whether there were any abrupt changes in the absorption of the more concentrated solutions of the series, because the spectrograms of Plates III(*c*) and VI., seemed to indicate a change of this kind. In the spectroscope the solution of concentration 1.224 appeared to transmit a spectrum which commenced at about 0.690 μ, rose gradually to a maximum of transmission, then decreased to about half the maximum intensity near 0.500 μ and, finally, faded away very gradually to zero value in the neighborhood of 0.447 μ. This type of variation in intensity, which is likewise characteristic of the solution of concentration 1.399, is shown correctly by the photographic strip next to the last, both on Plate III(*c*) and on Plate VI., only in so far as a weak prenumbra is indicated for the green and blue, but the eye did not detect a maximum of general absorption followed by slight increase in intensity of transmission as shorter and shorter wave lengths were observed, as would be inferred from the photographic strip in question.

Furthermore, the spectrum of the most concentrated solution of the set began at about 0.680 μ, rose slowly to a maximum of transmission at 0.608 μ, decreased gradually for a certain distance, then fell off rather abruptly near 0.545 μ and, finally, faded away to invisibility in the vicinity of 0.495 μ. The colors which were transmitted clearly enough to be recognized, *i. e.*, bright red, orange, yellow and green, were greatly weakened in intensity as compared with that of the light incident upon the absorbing layer of solution.

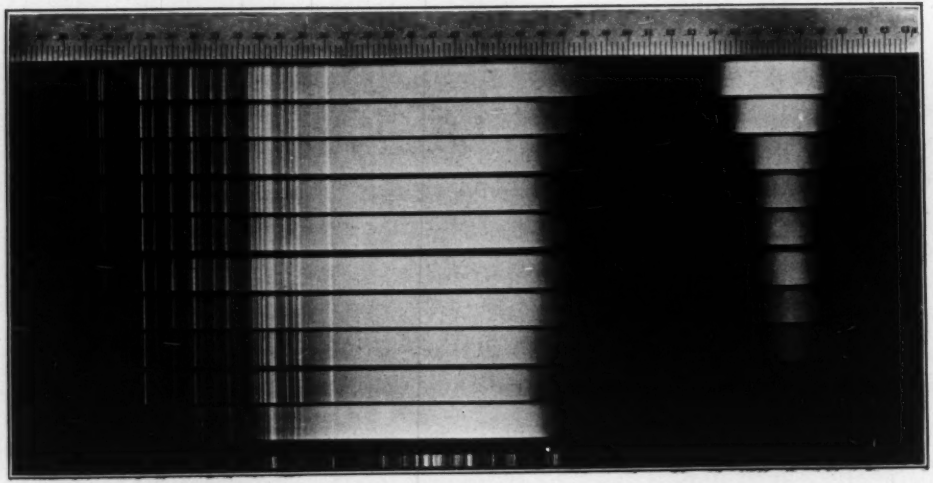
The region of very weak transmission between 0.545 μ and 0.495 μ was not shown by the negative from which Plates III(*c*) and VI. were reproduced. The conclusion to be drawn, then, is that there was no abrupt change in the general characteristics of the regions of absorption and of transmission of the several solutions of copper bromide studied, and that the lack of complete agreement between the results obtained, on the one hand by the photographic method, and on the other by observations in the case of the two solutions of greatest concentration, was due to the fact that certain portions

of the spectra transmitted were of too feeble intensity to affect the photographic film or plate either at all, or in a correct manner. Thus, the case of copper bromide furnishes a good illustration of the desirability, if not of the necessity, in general, of supplementing photographic work by eye observations.

Cobalt Chloride and Calcium Chloride.—(See Plates VIII., IX(*a*) and IX(*b*), the last two are reduced to three-fourths of the original size.) The spectrogram of Plate VIII. will be first discussed. The concentration of the cobalt chloride in all of the solution is a constant, 0.271. The concentrations of the calcium chloride were 0.000, 1.676, 2.514, 2.724, 2.849, 2.919, 3.007, 3.128, 3.336 and 3.765. These solutions were made up so as to show successive color changes which, judged by the eye, were as uniform as possible. The colors themselves varied from clear red to deep blue, passing through intermediate shades of garnet, purple, violet, etc.

The strip corresponding to the solution that contained no calcium chloride, appears next to the numbered scale, while the strip associated with the solution which had the greatest concentration in calcium chloride, lies closest to the comparison spectrum. The depth of the cell was 1.41 cm.

These regions of absorption are shown by the spectrogram. One of these is in the extreme ultra-violet, another is in the green, and a third is in the orange and red. The solution of cobalt chloride alone was unusually transparent to short waves of light, transmitting the spark line at 2265.1. The negative showed no shorter wave lengths. The band in the ultra-violet gradually extended to longer waves, as the concentration of calcium chloride increased. For example, the ninth solution transmitted the line of wave length 2558.0, but nothing more refrangible, and the continuous background did not persist quite as far as to the spark line last mentioned. The line spectrum of the strip adjacent to the spark scale is not comparable with the other strips, because the Leyden jar broke down in the course of the exposure. This accident had no influence, of course, on that part of the tenth strip, which was obtained by the use of the Nernst filament. The marked lack of intensity of the comparison spectrum was due to the



Platę VIII.

same break. The band in the green extended from about 0.505 μ to 0.530 μ, as shown by the negative for the solution containing no calcium chloride. This band widened out more and more as the concentration of the calcium chloride increased. At the same time general absorption was present on the orange side of the band, and not on the blue side. This fact, together with the one to be discussed below, in connection with the eye observations, namely, that there were bands of continually increasing width in the red, accounts for the change in the resultant color from red to blue when the calcium chloride was added to the solution of cobalt chloride.

Plate IX(*a*) shows the variation of the absorption of solutions of cobalt chloride and calcium chloride, when the successive increments of concentration were all equal. The electrical conductivities of these solutions were also measured. The constant concentration of the cobalt salt was 0.271 and the concentrations of the calcium chloride were 0.000, 0.325, 0.650, 0.974, 1.299, 1.624, 1.950. The common difference used in the calculation was 0.3248. The concentration of mother solutions of cobalt and of calcium chloride were, respectively, 2.71 and 4.06 N. The solution which contained the greatest amount of calcium chloride has its photographic strip adjacent to the comparison spectrum. The depth of the cell was the same as for Plate VIII.

The region of absorption in the ultra-violet widened out from 2194.7 to about 0.245 μ, when the extreme strips were measured. The limits of the band in the green increased linearly with the like change in the concentration of the calcium chloride. Also the centre of this band remained at the same wave length 0.518 μ for the 7 solutions under consideration.

Plate IX(*b*) gives the absorption spectra of another set of solutions containing the chlorides of cobalt and of calcium. These solutions were made up of such concentrations as to contain the same number of chlorine atoms as the corresponding solutions of a set in which aluminium chloride was the dehydrating agent, instead of calcium chloride. The reasons for this will be discussed later, when the facts about the spectra

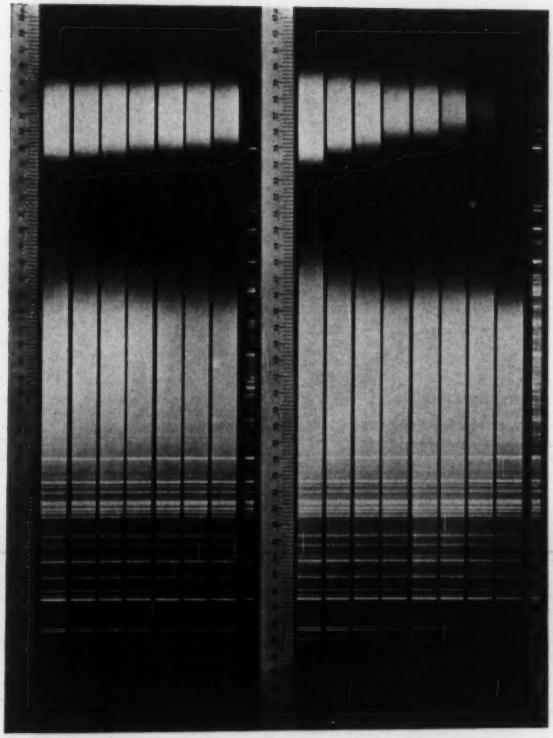
of aluminium chloride are given. Plate IX(*b*) supplements Plate IX(*a*) from the standpoint of concentrations, and also because of the circumstance that the solutions of both of these spectrograms have their conductivity data collected in one table and in a single curve in a later section. The concentration of the cobalt chloride was 0.271, as before, and the concentrations of the calcium chloride were 0.000, 1.676, 2.091, 2.515, 2.671, 2.830, 3.143, 3.555. Therefore, the differences of first order were 1.676, 0.415, 0.524, 0.156, 0.159, 0.313, 0.412. The depth of the absorbing layer, the times of exposure, and the relative positions of the photographic strips are the same for Plate IX(*b*) as for Plate IX(*a*). The negative for IX(*b*) shows a faint trace of the spark line at 2194.7 and 2573.1 for the strips associated respectively with the solutions of least and greatest concentration in the calcium salt. The continuous background does not extend quite as far as the wave lengths just given, especially in the case of the most concentrated solution. The general absorption in the yellow and orange is brought out clearly by the eighth strip. The question as to how much of the absorption in any given mixture of solutions, is to be ascribed to the colored salt, and how much is due to the dehydrating agent, will be taken up immediately after the other matters pertaining to the solutions containing cobalt chloride, together with calcium chloride, calcium bromide, or aluminium bromide shall have been discussed.

The most important facts brought out by the observations of the bands in the orange and red were the following: It is not necessary to give here the data relative to the band in the green, since they confirm in detail the results obtained photographically, and the latter is shown by the spectrograms.

The solutions studied with the spectroscope were the ones which accompany Plate VIII. The depth of cell used was 2.5 cm. With distilled water in the cell the red end of the spectrum appeared to begin at about 0.775 μ. The solution containing only cobalt chloride, as well as the one having the concentration 1.676, showed no absorption in the red. For the solution of concentration 2.514 of the calcium salt, 2

Plate IX(a).

Plate IX(b).



very faint flutings of intensity showed their maxima of absorption at 0.697 μ and 0.661 μ. By moving the spectrum across the field of view, it was just barely possible to see 2 extremely faint bands which were quite narrow, and which were situated at the shorter wave length side of the band at 0.662 μ. They were too faint, however, to set upon with the cross-hair. The next solution in order of concentration, 2.274, began to transmit faintly at 0.770 μ. The bands at 0.697 μ and 0.661 μ were more intense than before. A faint band appeared at 0.624 μ and a very faint one at 0.609 μ. An extremely faint, narrow band between the two just mentioned, could be seen with great difficulty.

A general idea of the appearance of the successive regions of transmission and absorption, for the solution of concentration 2.849, is given in Fig. 8 (*a*). The abscissae denote wave lengths and the ordinates show estimated intensities of transmission. The centres of the red regions of greatest transparency were, respectively, 0.726 μ and 0.675 μ. One absorption band was at 0.697 μ and the centre of the next band was at 0.661 μ. The entire region from 0.767 μ to beyond 0.660 μ had the appearance of a weak flat band with 2 maxima of absorption, the one at 0.697 μ and the other at 0.661 μ superposed upon it. The absorption at 0.697 μ was more intense than at 0.661 μ. Beyond 0.661 μ the general transmission was uniformly strong, but not as intense as when the cell contained water alone. The narrow band at 6045 was very faint; the next narrow band had the position given by 6245. This band was slightly more intense than the one at 6095. The last 2 bands had about the same width. The spectrum of the solution whose concentration in calcium chloride was 2.919, did not differ enough from that of the solution just discussed to merit further comment. For the solution of concentration 3.007 the band at 0.697 extended from 0.706 μ to 0.686 μ. The bright region lying between the bands at 0.661 μ and 6405 began at 0.655 μ, *i. e.*, the band at 0.661 μ ended rather abruptly at 0.655 μ. In all other particulars the spectrum of this solution was qualitatively similar to the spectra of the two preceding solutions.

The contrasts were more pronounced for the solution of concentration 3.128 than for any of the solutions containing

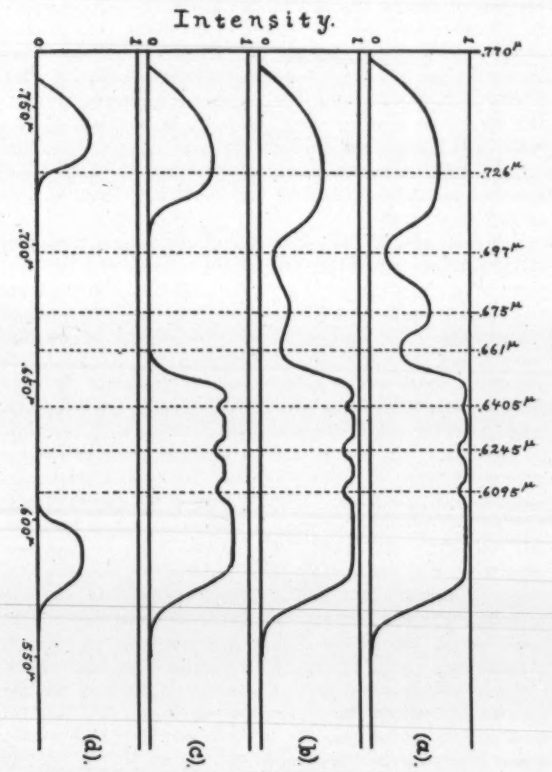


Fig. 8.

smaller amounts of the dehydrating agent. The spectrum had gradually changed to the form suggested by Fig. 8

(*a*). The maxima of absorption had not changed their wave lengths. The transmission between 0.72 μ and 0.66 μ had become so weak that it was difficult to distinguish the maximum at 0.697 μ.

The bands at 0.697 μ and 0.661 μ had coalesced completely for the solution of concentration 3.336 of the calcium chloride; in other words, the region of weak transmission at 0.675 μ had entirely disappeared [*vide* Plate VIII(*c*) . The resultant wide band extended from 0.714 μ to 0.654 μ with rather abrupt boundaries. The narrow bands at 6245 and 6095 had increased appreciably in depth, and the regions of transmission between 6610, 6405, 6245 and 6095 were much weaker, *i. e.*, the bands were joined by strong general absorption.

The solution which contained the largest amount of the dehydrating agent showed only one intense band in the red [*vide* Plate VIII(*d*)]. This band comprises the interval from 0.724 μ to 0.603 μ. The brightest spot of transmission in the red was at about 0.739 μ. Transmission in the yellow-green was noticeably weakened, and the next region of selective absorption commenced near 0.578 μ, increased to totality at 0.567 μ and then began to fade away again at 0.465 μ. All the spectra of the several solutions seemed to begin at the same wave length, namely at 0.770 μ, *i. e.*, there was no evidence of selective absorption in the extreme red.

The observed freezing points of aqueous solutions containing both cobalt chloride and calcium chloride are tabulated below. Certain associated data are also given, but the interpretation of the tables will be deferred to a later section, in which the general bearing of all the experimental facts on the hypothesis of hydrates will be discussed.

Table I.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $CaCl_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaCl_2$ alone were present.	5. Molecular lowering of freezing-point if $CaCl_2$ alone were present.	6. Molecular lowering of freezing-point for $CoCl_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.162(3)	2°.340(5)	0°.975	6°.02	4°.92	1°.10
0.271	0.325(3)	3°.400(5)	2°.035	6°.26	5°.05	1°.21
0.271	0.650(3)	6°.130(5)	4°.765	7°.33	5°.55	1°.78
0.271	0.974(3)	9°.115(5)	7°.750	7°.96	6°.29	1°.67
0.271	1.299(3)	12°.25(6)	10°.88	8°.38	7°.06	1°.32
0.271	1.462(3)	14°.00(6)	12°.63	8°.64	7°.38	1°.26
0.271	1.624(3)	16°.5(6)	15°.13	9°.32	7°.88	1°.44
0.271	1.676(2)	16°.2(4)	14°.83	8°.85	8°.03	0°.82
0.271	1.950(3)	23°.0(6)	21°.63	11°.09	9°.03	2°.06
0.271	2.091(2)	21°.7(4)	20°.33	9°.72	9°.32	0°.40
0.271	2.515(2)	29°.2(4)	27°.83	11°.06	10°.90	0°.16
0.271	2.671(2)	34°.5(4)	33°.13	12°.40	11°.53	0°.87
0.271	2.830(2)	39°.0(4)	37°.63	13°.30	12°.32	0°.98
0.271	3.143(2)	47°.0(4)	45°.63	14°.51	13°.81	0°.70
0.271	3.555(2)	?	. .	. .	. .	. .

The solutions whose concentrations are marked (2) or (3) were made up respectively on November 21 and on December 11, 1905. The freezing point lowerings indicated by (4), (5) or (6) were measured on December 7, 1905, February 16 and February 21, 1906. The arithmetical mean of the numbers in the last column, which correspond to solutions for which either 66 or 71 days elapsed between the times when the solutions were made up and when their freezing point lowerings were determined, is 1.48. The like mean for the remaining solutions, which were delayed 15 days, is 0.655. These two numbers show both that the solutions underwent a change with time and that the number of effective particles in the solutions increased, that is, marked hydrolysis took place. Compare, especially, the numbers in the seventh column associated with the concentrations 1.950 and 2.091.

[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, 33, 546 (1905).

The solution of concentration 3.143 was dark blue at room temperature but red near its freezing point. This phenomenon, however, has been observed often before. The most concentrated member of the series tabulated not only turned red, but the salt separated out when an attempt was made to determine its freezing point lowering.

The next table contains the electrical conductivities, at 0°, of the solutions of cobalt chloride and calcium chloride. The data are expressed in reciprocal ohms and reciprocal centimeters.

Table II.

Concentration of $CaCl_2$.	Conductivity.	Concentration of $CaCl_2$.	Conductivity.
0.000	0.02220	1.950	0.10886
0.162	0.03449	2.091	0.10958
0.325	0.04493	2.515	0.11653
0.650	0.06415	2.671	0.11512
0.974	0.07831	2.830	0.11387
1.299	0.09113	3.143	0.10789
1.462	0.09964	3.555	0.09755
1.624	0.10363	. .	. . .

Since the data for the electrical conductivities of standard solutions are usually expressed in terms of the reciprocal of Siemens' mercury unit, at least in books on physical chemistry, it may not be superfluous to explain how the reduction to reciprocal ohms and reciprocal centimeters is effected. The ratio of the Siemens' unit of *resistance* to the ohm is as 1 : 1.063, hence, to change the number representing the value of the *conductivity* of a given solution from reciprocal Siemens' units to reciprocal ohms the number must be multiplied by 1.063. In certain cases the reduction factor is 1.069. Further, reduction to reciprocal centimeters is accomplished by dividing the number expressing the conductivity in reciprocal ohms by the product of one thousand into the "volume" of the solution. For illustration, for 0.02 N aqueous solution of potassium chloride at 25° the conductivity in reciprocal Siemens' units is 129.7; therefore, the conductivity in reciprocal ohms and reciprocal centimeters equals $\frac{129.7 \times 1.063}{1000 \times 50} = 0.002757 = K_{25}$. Since for one and the same conductivity

cell, at the same temperature, the ratio of the specific conductivities of any two solutions is, by definition, equal to the inverse ratio of the ohmic resistances, it is only necessary to determine successively the resistances in the same cell and at constant temperature, of a standard solution and of a solution to be tested, and then to multiply the specific con-

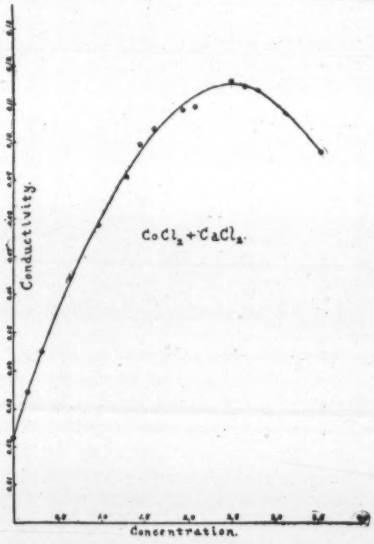


Fig. 9.

ductivity of the standard solution by the ratio of the ohmic resistance of the standard solution to the ohmic resistance of the solution under investigation, in order to find the value of the specific conductivity of the solution in question. In obvious notation,

$$K_x = K \frac{R_s}{R_x} \text{ohm}^{-1}, \text{ cm.}^{-1}.$$

Fig. 9 shows, graphically, the functional relation between the electrical conductivity and the concentration of the solutions under consideration. The abscissae denote the concentrations of the calcium chloride, and the ordinates give the corresponding conductivities in the units specified above. It is interesting to notice that the conductivity rose to a maximum value and then decreased, as the quantity of the dehydrating agent in the solutions increased. The concentration corresponding to the maximum conductivity was about 2.5. The concentration of the cobalt chloride was the constant 0.271.

Cobalt Chloride and Calcium Bromide.—(See Plate X. which is reduced to three-fourths of the original size). The cobalt chloride had the concentration 0.271 in all of the solutions of the set now under consideration. The concentrations of the calcium bromide were 0.000, 0.189, 0.379, 0.568, 0.757, 0.947, 1.136, 1.515, 1.893, 2.272, 2.650, 3.143, 3.313, 3.597, 3.938, 4.260. The first 6 increments of concentration were each 0.189, the next 4 separately equaled 0.379, and the remainder had the values 0.493, 0.170, 0.284, 0.341 and 0.322. The concentration of the mother solution of calcium bromide was 4.733. The solutions containing calcium bromide had colors similar to the solutions in which calcium chloride was present, namely, all shades from red to intense blue. The photographic strips succeed one another from the side of the spectrogram adjacent to the numbered scale, to the edge adjoining the spark spectrum, in the order of increasing concentration of calcium bromide. The half-films were not developed simultaneously in this particular case. The depth of the cell was 1.41 cm. The spectrogram shows, qualitatively, the same regions of absorption for the solutions made up with calcium bromide, as had been described above for the solutions containing calcium chloride. The slit of the spectrograph was narrower than usual, and this accounts for the partial absence of continuous background in the ultra-violet. The negative recorded the line at 2265.1 as transmitted by the solution in which no dehydrating agent was present. No shorter wave sensibly affected the film. The region of absorption in the ultra-violet,

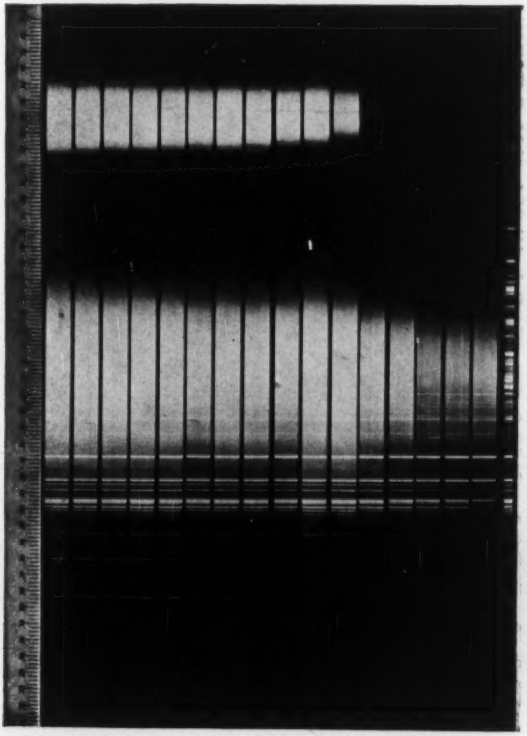
extended to longer and longer wave lengths as the amount of bromide in the solutions became greater and greater. The shortest wave transmitted by the most concentrated solution, as shown by the negative, had a length of 3261.2 A. U. The middle of the band in the green has approximately the position given by 0.518 μ. The strips pertaining to the first 11 solutions show that the width of the band just mentioned varied almost linearly with the like change in concentration of the calcium chloride. This band, according to the negative for the most concentrated solution, possessed complete absorption from 0.460 μ to wave lengths beyond the nearer end of the spectrogram. The presence of general absorption in the yellow orange is clearly brought out by the photographic strips beginning with the twelfth and ending with the sixteenth.

Eye observations on typical solutions of the set under consideration, were made with the aid of the double cell, and the most important changes in absorption noted were as follows. The comparison of the first and sixth solutions showed no appreciable difference in the orange and red portions of the parallel spectra. The data relative to the band in the green need not be repeated, since they can be obtained in great detail from Plate X.

The sixth and ninth solutions gave spectra of sensibly the same intensity, except in the region of the absorption band in the green. No trace of the bands in the orange and red could be seen in the preceding spectra.

The twelfth solution absorbed the extreme red a little more than the ninth. More specifically, if it be said that the spectrum of the former began at 0.700 μ then the corresponding number for the latter would be 0.736 μ. The narrow bands at 6245 and 6045 (Fig. 8 (*a*)) could only be seen for the twelfth solution, by moving the spectrum across the field of view of the telescope. The axes of the collimator and telescope were fixed at right angles to each other, and the spectrum was moved by rotating the prism by means of the wave length drum.

Plate X.



The bright regions of transmission were approximately of the same intensity throughout. The thirteenth solution dimmed almost the entire spectrum a little more than the twelfth, and it showed faintly the band at 6405 and more distinctly the bands at 6610, 6245 and 6095. The former solution showed almost complete absorption of all visible light of wave length greater than 0.687 μ. The absorption in the same region was not so intense for the twelfth solution. Both solutions transmitted the violet with about the same intensity.

The fourteenth solution absorbed completely all the red as far as 0.632 μ, thus including the narrow band at 6405. The yellow was much less intensely transmitted by the more concentrated solution than by the weaker one. A change similar in kind, but not in degree, appeared in the indigo and violet.

Only a short, comparatively faint region of yellow was transmitted by the fifteenth solution. If it be stated that the fourteenth solution absorbed everything visible beyond 0.632 μ, then the corresponding number for the fifteenth solution must be 0.619 μ.

The spectrum of the less concentrated solution of the pair was much brighter in the yellow than that of the more concentrated solution.

The most concentrated solution of the series did not transmit the faintest trace of orange or yellow light. Its spectrum extended from about 0.460 μ to the ultra-violet. The intensity of violet transmitted by the fifteenth and sixteenth solutions appeared the same for the 2 spectra.

The freezing point lowerings for the solutions containing both cobalt chloride and calcium chloride are given in the following table:

Table III.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $CaBr_2$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $CaBr_2$ alone were present.	5. Molecular lowering of freezing-point if $CaBr_2$ alone were present.	6. Molecular lowering of freezing-point for $CaBr_2$ in H_2O alone.[1]	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.189	2°.703	1°.338	7.09	5.19	1.90
0.271	0.379	4°.276	2°.911	7.68	5.37	2.31
0.271	0.568	5°.627	4°.262	7.50	5.63	1.87
0.271	0.757	7°.600	6°.235	8.24	5.76	2.48
0.271	0.947	9°.732	8°.367	8.84	6.07	2.77
0.271	1.136	11°.25	9°.88	8.70	6.95	1.75
0.271	1.515	15°.0	13°.63	9.00	8.70	0.30
0.271	1.893	21°.6	20°.23	10.69	9.58	1.11
0.271	2.272	29°.5	28°.13	12.38	11.84	0.54
0.271	2.650	40°.0	38°.63	14.58	13.84	0.74
0.271	3.143	56°	54°.6	17.37	16.26[2]	1.11
0.271	3.313	65°	63°.6	19.20	(17.09)[2]	(2.11)
0.271	3.597	65° (?)	. .	. .	. .	. .
0.271	3.938	(?)	. .	. .	. .	. .
0.271	4.260	(?)	. .	. .	. .	. .

The solutions whose concentrations were between 0.189 and 1.136 inclusive of the limits, had their freezing point lowerings determined 74 days after they were made up, whereas the corresponding time for each of the remaining solutions of the series was 14 days. The average value of the first 6 numbers in the last column of Table III. is 2.18, and the mean of the next 5 numbers is 0.76. Hence, the same increase with time of the number of particles which took part in the lowering of the freezing point was observed for the solutions containing both cobalt chloride and calcium chloride, as was pointed out in connection with Table I. for the solutions containing the chlorides of cobalt and of calcium. The solutions having the concentrations 3.143, 3.313 and 3.938 became very viscous jellies near their freezing points and, therefore, it was not possible to determine the temperatures of these points

[1] Interpolated from the table given by Jones and Bassett: THIS JOURNAL, **33**, 550 (1905).

[2] Extrapolated.

with even a reasonable degree of accuracy. On this account 2 of the numbers in Table III. are enclosed in parentheses. Salt separated out when the attempt was made to ascertain the order of magnitude of the freezing point lowering produced by the most concentrated solution. All of the most concentrated solutions were blue at room temperature, but they were of the characteristic cobalt rose color in the neighborhood of their respective freezing points.

Table IV. gives the electrical conductivities at 0° of the solutions of cobalt chloride and calcium bromide. As formerly, the conductivity data are expressed in reciprocal ohms and reciprocal centimeters:

Table IV.

Concentration of $CaBr_2$.	Conductivity	Concentration of $CaBr_2$.	Conductivity.
0.000	0.02220	2.272	0.12252
0.189	0.03994	2.650	0.12101
0.379	0.05465	3.143	0.11014
0.568	0.06308	3.313	0.10470
0.757	0.07412	3.597	0.09496
1.136	0.09244	3.938	0.08313
1.515	0.10643	4.260	0.07005
1.893	0.11913	. .	. . .

The dependence of the conductivity upon the concentration of the calcium bromide is shown graphically by Fig. 10. The abscissae denote concentrations of the dehydrating agent and the ordinates give the corresponding conductivities. The concentration of the cobalt chloride was the constant 0.271. The maximum in the curve for the solutions containing the bromide was even more pronounced than it was for the curve pertaining to the solutions of the chloride of calcium. Moreover, these 2 maxima occur at, roughly, the same concentration, *i. e.*, at about 2.5 and 2.4 for the solutions containing the chloride and bromide, respectively.

Cobalt Chloride and Aluminium Chloride.—(See Plates XI(*a*) and XII. The first is reduced to three-fourths of the original size.) The concentrations of the aluminium chloride in the solutions corresponding to Plate XI(*a*) were 0.000, 1.118, 1.394, 1.676, 1.781, 1.887, 2.100 and 2.459. The increments

of concentration were 1.118, 0.276, 0.282, 0.105, 0.106, 0.213, 0.359. The concentration of the cobalt chloride throughout was 0.271.

The concentration of the mother solution of aluminium chloride was 2.75. The solutions made up from this mother solution, and containing cobalt chloride, had colors similar

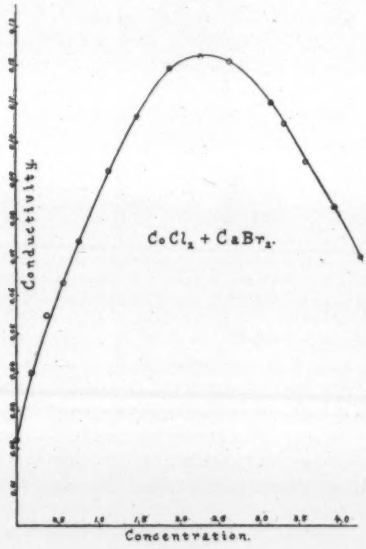


Fig. 10.

to those of solutions in which either the bromide or chloride of calcium was present, namely, all shades from red to intense blue. The photographic strips succeed one another from the side of the spectrogram adjacent to the numbered scale, to the edge contiguous to the spark spectrum, in the order of increasing concentration of the dehydrating agent. The depth of the cell was 1.41 cm. The spectrum shows, qualitatively,

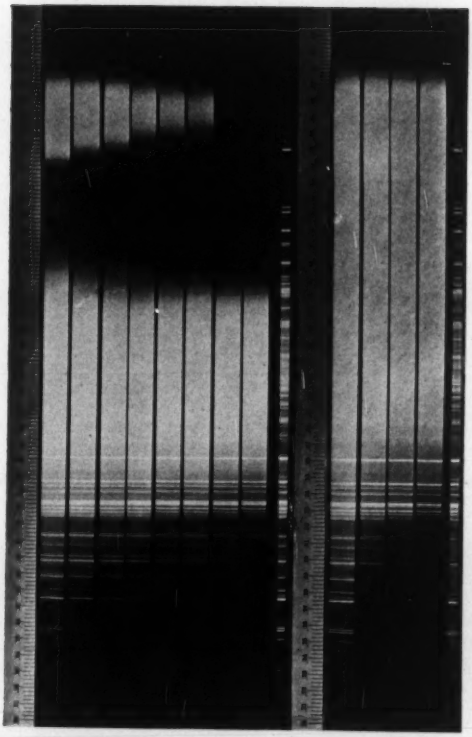
the same regions of absorption as have been noted for all of the preceding series or sets of solutions containing cobalt chloride.

The negative recorded the line at 2265.1 as the most refrangible radiation transmitted by the solution which contained none of the aluminium chloride. The most concentrated solution transmitted a trace of the line of wave length 2748.7, but the continuous background was completely absorbed beyond 0.288 μ. The absorption band in the green was at about 0.518 μ. The greatest wave length for light transmitted at the blue side of this band, for the most concentrated solution, was given by the negative as 0.484 μ. The seventh and eighth photographic strips, especially, show general absorption in the orange.

A few attempts were made to find out whether any simple relation might exist between 2 solutions having apparently the same color, the one containing calcium chloride and the other aluminium chloride. Except for the extremely concentrated solution, it was found that, as a first approximation, 2 solutions of the kind just mentioned were isochromatic when they contained equal numbers of chlorine atoms. The number before each comma in the following sequence, denote the concentration of the solution containing the chlorides of cobalt and calcium, and the number immediately following the comma in question signifies the concentration of the corresponding solution containing the same amount of cobalt chloride, and such an amount of aluminium chloride as to possess the same number of chlorine atoms as the solution whose concentration precedes the comma. The pairs are: 1.676, 1.118; 2.091, 1.394; 2.515, 1.676; 2.671, 1.781; 2.830, 1.887; 3.143; 2.100; and 3.555, 2.370. As far as the eye could tell the members of each pair of solutions had the same color when they were viewed in their bottles. All of the calcium chloride solutions and all of the aluminium chloride solutions except the most concentrated one, have their absorption spectra produced by Plates IX(*b*) and XI(*a*), respectively. To make the comparison easier and more direct, the members of the first, third, sixth and last pairs of solu-

tions were photographed side by side and in quick succession. The resulting spectrogram is shown on Plate XII. Counting from the side of the plate nearest to the numbered scale, the first, third, fifth and seventh photographic strips correspond to the solutions which contain calcium chloride, and the remaining strips pertain to the solutions which contain aluminium chloride. The depth of the cell was 1.41 cm. In the ultra-violet the solutions which contained the aluminium salt showed much stronger absorption than those which were made up with the calcium salt. On the other hand, the band in the green is a little more intense for the solutions which contain calcium chloride than for the solutions of the other set. That this difference, however, is not very appreciable is readily seen from Plate XII. Due to the presence of a small quantity of some impurity, the mother solution of aluminium chloride had a slight color in layers of 5 or more cm. in thickness. The facts brought out by the spectrogram of the mother solution of aluminium chloride are given below: Two strips were photographed, the one corresponding to a depth of 15.1 cm. and the other to a depth of 1.41 cm. The Nernst filament was given an exposure each time of 2 minutes and the spark was run for 1.5 min. The negative shows complete absorption of all the ultra-violet and violet as far as 0.415 μ for the deeper layer, and the entire strip is relatively faint and underexposed. In fact, the photographic impression fades away about 230 A. U. farther from the longer wave length end of the negative for the deeper layer than for the shallower one. The faintest trace of the spark line at 2558 was transmitted by the shallow layer of solution; also the line at 2748.7 was barely recorded on the negative. The continuous background bagan at about 0.288 μ and did not attain its full intensity for wave lengths shorter than 0.325 μ. Eye observations completely confirm photographic results in the visible region, especially with regard to appreciable absorption of the violet even for a depth of 5.3 cm., and marked general absorption through the entire spectrum for a depth of 15.1 cm. It was, therefore, evident that the mother solution of aluminium chloride possessed both selective and general

Plate XI(a). Plate XI(b).



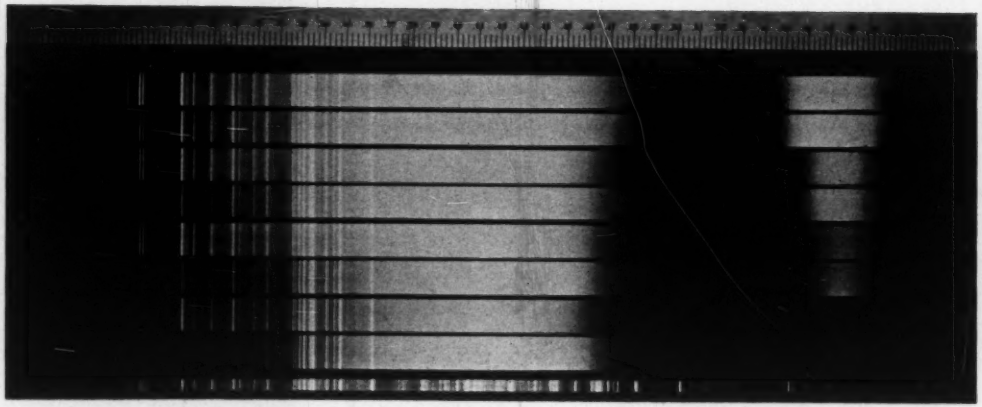


Plate XII.

absorption, which were certainly not negligible for long columns of solution, and perhaps not inappreciable for such short columns as 1.41 cm. Consequently, the differences in ultra-violet absorption shown by Plate XII. for the successive pairs of solutions, may be due to the strong absorption in this region of the aluminium chloride, and not to the presence of the cobalt chloride even alone or as influenced by the dehydrating agent.

Before giving the facts obtained by eye observations, by freezing point and conductivity measurements, with the solutions containing the chlorides of cobalt and of aluminium, it may not be out of place to present the salient points brought out by the photographic comparison of the relative intensities and extents of absorption exerted by the mother solution of calcium chloride, calcium bromide and aluminium bromide. The spectra are shown by Plate XI(*b*). The concentration of the calcium chloride solution was 4.51, that of the bromide was 4.236, and that of the aluminium salt was 2.75. The strip nearest to the numbered scale corresponds to distilled water. The next strip pertains to the solution of calcium chloride, the third strip is due to the aluminium chloride, and the strip adjacent to the comparison spectrum is that of calcium bromide. The depth of the cell was 1.41 cm. The negative indicated no absorption at all for the distilled water, in other words, the zinc line at 2024.2 was recorded. The calcium chloride transmitted a trace of the strong cadmium line at 2265.1. This solution absorbed practically all of the continuous background between 0.280 μ and 0.202 μ. The mother solution of aluminium chloride transmitted precisely the same lines as did the solution of calcium chloride, but the former absorbed and weakened the continuous background a good deal more than the latter. When the concentrations of these 2 solutions are taken into account, the relatively great absorbing power of the aluminium salt for the very short waves becomes evident at once. The strong emission line at 2748.7 was weakly transmitted by the solution of calcium bromide, but the continuous background was almost completely absorbed beyond 0.313 μ. Since the concentration

of the calcium bromide solution was somewhat less than that of the calcium chloride, the second and fourth photographic strips show, conclusively, how very much stronger the absorption of the bromide is than the chloride for the short light waves. For the depths used in the visible region the 3 solutions in question exerted no appreciable absorption.

In the light of what has just been explained, a comparison of the spectrograms of Plates II., IX(*a*), IX(*b*), X, XI(*a*) and XI(*b*) leads to the conclusion that, in general, the absorption of the ultra-violet light by the cobalt chloride is marked, to some extent, by the superposition of the greater absorption of the dehydrating agent in a given solution. Therefore, the absorption bands in the visible spectrum are better criteria for the behavior of the cobalt salt in the presence of some one of the dehydrating agents than the region of absorption in the ultra-violet. It does not seem necessary to enter into minute details relative to the general principles just stated.

Eye observations on the absorption spectra of the solutions which contained the chlorides of cobalt and aluminium, led to practically the same results as were obtained with the other 2 dehydrating agents under investigation. The chief characteristics of these spectra are shown by the 4 curves of Fig. 8. The depth of column used was 2.5 cm. The solutions of concentration 1.118 and 1.394, in the aluminium salt, did not show even the faintest traces of discrete bands in the red. The entire set of 5 bands could barely be distinguished with the solution of concentration 1.676. The solution of concentration 1.781 has its system of bands represented fairly well by Fig. 8 (*a*) except that the band at 6405 was difficult to see. The bands 6405, 6245 and 6095 were relatively intense, but not very clear cut and well defined for the solution of concentration 1.887. Fig. 8 (*c*) gives an idea of the regions of transmission and absorption for the solution of concentration 2.100. For this solution the bands at 0.697 and 0.661 had coalesced and the resultant region extended from 0.713 μ to 0.653 μ. A deep shadow joined this region to the narrow band at 6405. The bands at 6245

and 6095 were very intense. The width of the band at 6245 was about 55 A. U. A solution which is not included in the set photographed, having the concentration 2.340, showed the entire group of 5 bands as one single region of absorption, like that indicated by Fig. 8. (*d*). This region had the limits 0.724 μ and 0.599 μ. The transmission of light in the interval from 0.599 μ to the beginning of the band in the green was very weak. The most concentrated solution of the series transmitted faintly a narrow band of red. The coalesced group extended from 0.736 μ to 0.590 μ. The region of transmission in the yellow-green was very dim, and lay in the prenumbra of the absorption band whose maximum was near 0.518 μ. The absorption in the red and yellow was much more complete than for the most concentrated member of the series of solutions which contained calcium chloride.

The freezing point lowerings for the solutions containing both cobalt chloride and aluminium chloride are given in the following table:

Table V.

1. Concentration of $CoCl_2$ in the mixture.	2. Concentration of $AlCl_3$ in the mixture.	3. Observed freezing-point lowering of the mixture.	4. Lowering of freezing-point if $AlCl_3$ alone were present.	5. Molecular lowering of freezing-point if $AlCl_3$ alone were present.	6. Molecular lowering of freezing-point for $AlCl_3$ in H_2O alone.	7. Column 5 minus column 6.
0.271	0.000	1°.365	. .	. .	. .	. .
0.271	0.165	2°.692	1°.327	8°.08	5°.72	2.32
0.271	0.330	4°.35	2°.99	9°.06	6°.27	2.79
0.271	0.495	6°.26	4°.80	9°.70	7°.02	2.68
0.271	0.660	8°.71	7°.35	11°.14	7°.80	3.34
0.271	0.825	11°.4	10°.04	12°.17	8°.79	3.38
0.271	0.990	14°.6	13°.24	13°.37	9°.92	3.45
0.271	1.118	17°.5	16°.14	14°.44	10°.84	3.60
0.271	1.394	25°.6	24°.24	17°.39	13°.23	4.16
0.271	1.485	28°.9	27°.54	18°.55	14°.06	4.49
0.271	1.676	38°.0	36°.64	21°.86	15°.95	5.91
0.271	1.781	44°.0	42°.64	23°.94	17°.18	6.76
0.271	1.887	49°.0	47°.64	25°.2	18°.4	6.8
0.271	1.980	54°.0	52°.6	26°.6	19°.7	6.9
0.271	2.096	50 ?	. .	. .	. .	. .
0.271	2.370	. .	. .	. .	. .	. .
0.271	2.459	. .	. .	. .	. .	. .

When cooled by the mixture of ethyl alcohol and solid carbon dioxide the most concentrated solutions became very viscous, red jellies, which either undercooled about 20° and then became solid, or the salt separated out of the jelly. Hence, it was not possible to assign correct values to the freezing point lowerings of these solutions. With the exception of the second or third member, the numbers in the last column of Table V. become gradually larger as the concentration of the solution increases.

The electrical conductivities, together with the corresponding concentrations of the solutions containing cobalt chloride and aluminium chloride, are given in Table VI. The numbers in the second and fourth columns are expressed in reciprocal ohms and reciprocal centimeters:

Table VI.

1. Concentration	2. Conductivity.	3. Concentration.	4. Conductivity.
0.000	0.02220	1.485	0.06657
0.165	0.03845	1.676	0.06076
0.330	0.05050	1.781	0.05830
0.495	0.05924	1.887	0.05468
0.660	0.06577	1.980	0.05054
0.825	0.06889	2.100	0.04747
0.990	0.07078	2.370	0.03736
1.118	0.07204	2.459	0.03279
1.394	0.06887	. .	. . .

The data in the above table are plotted in Fig. 11. The abscissae denote concentration, and the ordinates signify conductivity. The mean curve has a decided maximum like the curves for the solutions containing calcium chloride and calcium bromide. There is this difference, however, between the curves of Fig. 11 and the other 2 curves, namely, that whereas the maximum of the curve associated with aluminium chloride corresponds to a concentration of about 1.1, the maxima for the other 2 dehydrating agents in question occur at the concentration 2.4 and 2.5.

When a sufficient quantity of water is added to a solution of cobalt chloride, which had previously been made blue by the admixture of a solution of some one of the 3 dehydrating

agents under investigation, the solution turns back to the characteristic cobalt red. It was thought that by adding water to a chosen solution of the given series, until the color of this solution became practically the same as that of the solution containing a somewhat smaller amount of the dehydrating agent, it might be possible to obtain some facts which would bear a quantitative relation to the hydrates formed

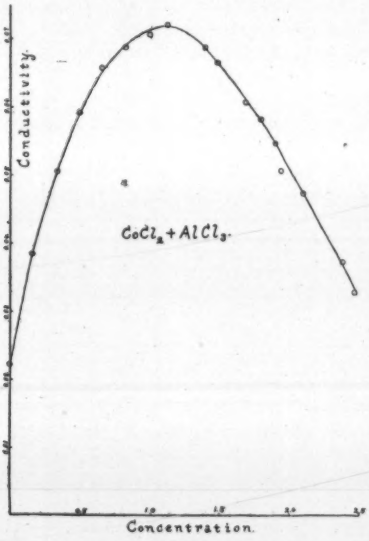


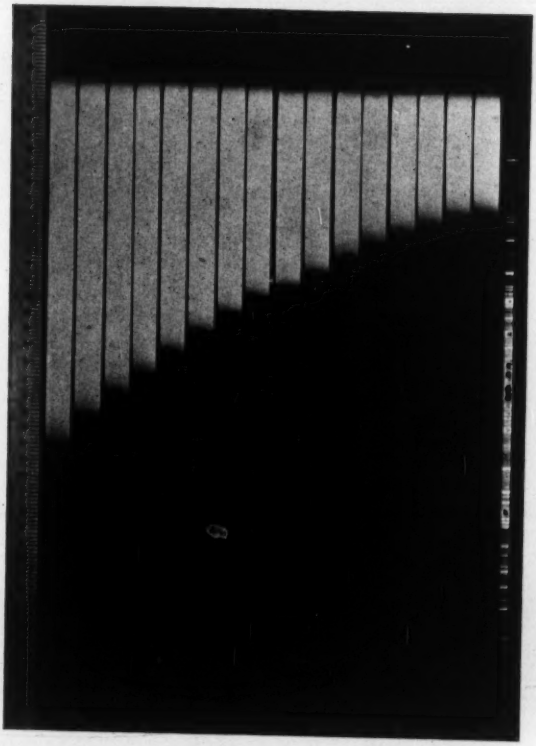
Fig. 11.

in the solutions. If it were possible to take infinitesimal steps these data might be obtained. But, obviously, such a process cannot be realized experimentally. In practice, either one of two difficulties presents itself: (*a*) the successive solutions differ so little in concentration, that the volume of water which has to be added to the more concentrated solution to bring its color to that of the less concentrated one, is too small

to be accurately measured unless undue precautions are taken. Moreover, 2 solutions of nearly equal concentrations differ so little in color as to make the error which necessarily arises in estimating that the colors have been made the same by the act of diluting, relatively great. (*b*) When the concentrations of 2 solutions differ by a reasonable amount, it is not possible to dilute the bluer solution until it assumes the same color as the less blue one, because the volume of water added so greatly increases the volume of the solution as to change the concentration of the cobalt chloride itself, quite independently of any change in the amount of hydration of this salt. In other words, the colors of the 2 solutions cannot readily be made the same under comparable conditions, when the concentrations differ very widely.

The matter under consideration was carefully tested for some of the solutions of cobalt chloride and aluminium chloride, as follows: The lower compartment of a double cell was filled with the less concentrated solution of a chosen pair. A measured volume (4 cc.) of the more concentrated solution was placed in the upper compartment of the cell. Then pure water was run into the upper solution from a burette, until the color in the 2 compartments appeared the same. The upper solution was, of course, made homogeneous. The volumes of water which were both insufficient and too great to dilute the more concentrated solution to the color of the less concentrated were noted, as well as the volume of water which was necessary to produce approximate equality of color. The mean of several trials was taken, In some cases the solutions were examined with the Hilger spectroscope. In this way it was possible to obtain data which are at least of the right order of magnitude. The results are given in Table VII. The first column gives the concentration of the solution to which the water was added. The second column gives in the same line the concentration of the solution which was used as the standard for color. The difference in the concentrations $(c_1 - c_2)$ is shown by the third column. The volume (V) of water necessary to produce equality of color

Plate XIII.



is given in the fourth column. The fifth column gives unit volume of water per unit volume of solution, per unit concentration of aluminium chloride and per unit change in concentration, *i. e.*, $\frac{v}{4c_1(c_1 - c_2)}$.

Table VII.

c_1.	c_2.	$c_1 - c_2$.	V. *cc.*	$\frac{V}{4c_1(c_1-c_2)}$.
1.485	1.394	0.991	0.260	0.48
1.676	1.485	0.191	0.470	0.37
1.781	1.676	0.105	0.180	0.24
1.887	1.781	0.106	0.210	0.26
1.980	1.887	0.093	0.145	0.20
2.100	1.980	0.120	0.155	0.15
2.370	2.100	0.270	0.350	0.14

The numbers in the last column show a definite decrease as the concentration of the dehydrating agent increases.

Copper Chloride and Calcium Chloride.— (See Plate XIII., which is reduced to three-fourths of the original size.) The concentration of the copper chloride in all of the solutions had a constant value 0.398. Concentrations of the calcium chloride were 0.0000, 0.271, 0.541, 0.812, 1.082, 1.353, 1.624 1.894, 2.165 2.435, 2.706, 2.977, 3.247, 3.518, 3.788, 4.041. All the increments of concentration have the value 0.2706, except the last one, and its value is 0.253. The concentration of the mother solution of calcium chloride was 4.51. The colors of solutions commenced with clear blue for the most dilute solutions, and passed through the various shades of greenish blue, bluish green, clear green and yellowish green and the concentration of the calcium chloride increased until a deep greenish yellow color was reached.

[The remainder of this paper, together with one relating to non-aqueous solvents, will appear in the March number of THIS JOURNAL.]

REPORT.

The Mechanism of Carbon Assimilation in Green Plants.

The nature of the processes whereby, in the sunlight, carbon dioxide is absorbed and oxygen exhaled by green leaves has aroused much interest in recent years. The action occurs on such an enormous scale and is of such prime importance in the organic world, that our very meagre knowledge of the steps involved has been annoying. Two most interesting articles by F. L. Usher and J. H. Priestley[1] have appered recently, which seem to throw much light on this perplexing question.

In 1870 Baeyer suggested that formic aldehyde is the first product of the decomposition of carbon dioxide in the plant. In 1877 Erlenmeyer[2] advanced an interesting theory of the mechanism of carbon assimilation. He found that lactic acid, on boiling with dilute sulphuric acid, decomposes into acetic aldehyde and formic acid. Similarly, glycollic acid yields formic aldehyde and formic acid. These reactions may be represented as follows:

$$\begin{matrix} CH_3CH(OH)|COOH \\ HO|H \end{matrix} = CH_3CHO + HCOOH + H_2O;$$

$$\begin{matrix} HCH(OH)|COOH \\ OH|H \end{matrix} = HCHO + HCOOH + H_2O.$$

Erlenmeyer believed that the decomposition of carbon dioxide occurs in an analogous way, so that the first products obtained would be formic acid and hydrogen peroxide. He also stated that it was not unthinkable that the formic acid undergoes a similar decomposition, resulting in the formation of formic aldehyde; hydrogen peroxide would have to be produced simultaneously in this change also.

$$\begin{matrix} HOCO|OH \\ H|OH \end{matrix} = HCOOH + H_2O_2;$$

$$\begin{matrix} HCO|OH \\ H|OH \end{matrix} = HCHO + H_2O_2.$$

The work of Usher and Priestley agrees in all details with the views of Erlenmeyer. Quite recently Bouilhac and Tréboux have shown that *Elodea* forms starch in the dark from a 0.001 per cent solution of formic aldehyde. Their work demonstrated the extreme toxicity of formic aldehyde.

The authors of the papers under review state that if formic aldehyde is produced, it must be very rapidly transformed

[1] P. Roy. Soc., *B.* 77, 369; 78, 318 (1906).

[2] Ber. d. chem. Ges., 10, 634 (1877).

into some physiologically inert substance and the hydrogen peroxide must be decomposed with the evolution of oxygen. They show the presence of catalase, the enzyme which decomposes hydrogen peroxide into water and oxygen, in the chloroplasts of plants belonging to 46 Natural Orders. They studied the production of formic aldehyde and the manner of its removal as follows: Since formic aldehyde must be so quickly removed in the living plant, they killed the *Elodea* by boiling it for 30 seconds and then exposed it to sunlight. In a few hours the plants were bleached and on dipping the leaves into a solution of rosaniline, decolorized with sulphur dioxide, a red color developed. This does not occur with the living *Elodea*. They attribute the bleaching of the chlorophyll to the accumulation of hydrogen peroxide, because the catalase is destroyed by the boiling. This experiment proved that the initial step in the assimilation of carbon is independent of living protoplasm and also proved that no enzyme is concerned in this step. It furthermore proved that, in all probability, formic aldehyde is produced. They then showed that exposure to the vapor of chloroform has almost the same effect as boiling, that is, on exposure to sunlight the leaves were bleached and formic aldehyde was again found. The formic aldehyde was further identified by distilling an extract of the leaves and obtaining anhydroformaldehydeaniline and also the tetrabrom derivative of hexamethylenetetramine. The fact that chloroform vapor prevents the polymerization of the formaldehyde proves, according to the authors, that this latter process depends on the vitality of the protoplasm and cannot be caused by an enzyme, as the latter substances are not rendered inactive by chloroform. Thus the first stage of carbon assimilation consists in the formation of formic aldehyde and hydrogen peroxide and this is effected by the chlorophyll and sunlight, independently of living protoplasm and enzymes. The hydrogen peroxide is decomposed into water and oxygen by the enzyme catalase, and if this fails to occur it bleaches the chlorophyll. The polymerization of the formic aldehyde is effected by the living protoplasm, but should this fail to occur, it destroys the catalase. In their second paper they show that by painting a thin layer of gelatin with a benzene solution of chlorophyll, a mechanism is obtained which, on exposure to sunlight, decomposes carbon dioxide into formic aldehyde and hydrogen peroxide. They further show that the white petals of *Saxafraga Wallacei*, which can form starch from very dilute solutions of formic aldehyde, when painted with the solution of chlorophyll in benzene, become capable of forming starch from carbon dioxide

in the sunlight. By making the gelatin layer alkaline in the experiments described above, they proved that formic acid is an intermediate product in the reduction of carbon dioxide to formic aldehyde. In this case only formic acid is produced and no formic aldehyde.

Finally, they proved the *Elodea* is capable of forming starch from formic acid in sunlight. Also, in this case, oxygen was given off, which proves that hydrogen peroxide must likewise be formed in the reduction, which would follow according to Erlenmeyer's view. For the interesting results of the authors on the decomposition of carbon dioxide by means of uranium compounds, in the sunlight, those interested are referred to the original articles.

A. S. LOEVENHART.

REVIEWS.

AMERIKANISCHES HOCHSCHULWESEN. EINDRÜCKE UND BETRACHTUNGEN. VON DR. W. BÖTTGER, Privatdozent an der Universität Leipzig. Leipzig: Engelmann. 1906. pp. 70.

The author of this pamphlet spent a year in this country as Research Associate in the Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology, and in this pamphlet he gives some of his impressions in regard to the *Hochschulwesen* of this country. Now the *Hochschule* is primarily a university in Germany, and if characterized as a technische *Hochschule* it is a Polytechnic Institute or an Institute of Technology. The methods in the two are quite different, though there are, of course, points of similarity. The question suggests itself: Does experience gained in an Institute of Technology, however excellent that institute may be, especially fit one to write on the conditions existing in the universities? It is not the purpose of this brief notice to discuss Dr. Böttger's book as a whole, but only to call attention to a few points referring mainly to the teaching of chemistry in America. The author says:

"In Amerika sieht man das Ziel des Hochschulunterrichts darin, die Leistungen der Durchschnittsmenschen zu erhöhen, während man bekanntlich in Deutschland das Hauptgewicht darauf legt, dass die Besten zu voller Entwicklung kommen können. Mir scheint, dass dieser Umstand den wesentlichsten Unterschied in den beiderseitigen Ansichten über die Ziele des Unterrichts an Hochschulen bildet."

This statement is largely true so far as the work of colleges and technological institutes is concerned; at least, I believe it to be true. If the author refers to the higher work, the

graduate work, of our universities, he is wrong. In this work every effort is made to secure the highest results for the best students. The reason why men who are not of the highest order find their way into the learned professions is that the demand is much greater than the supply.

On pages 30–32 an examination paper in chemistry, intended for candidates for the degree of Ph.D. at the Massachusetts Institute of Technology, is given. The paper is a good one, but hardly typical. It would have been much more instructive to give the examination papers for the degree of Ph.D. set in a dozen of our universities.

Under the head of "Die Organisation des Unterrichts" the illustrations are taken from the catalogue of the Massachusetts Institute of Technology. Again, it should be remarked, the plan of instruction described is not typical of American universities, though no doubt excellent in many respects.

The book will hardly be helpful to Americans, and, though interesting, it will prove somewhat misleading to Germans.

I. R.

RESEARCHES ON CELLULOSE. II. (1900–1905). By C. F. CROSS AND E. J. BEVAN. London, New York and Bombay: Longmans, Green & Co. 1906. pp. xii + 184.

The appearance, about 6 years ago, of the authors' first book on cellulose marked a distinct epoch in the chemistry of that substance As is well known, the services of the authors to the elucidation of the cellulose problem have not been confined to the literary side, their discoveries in the laboratory have been of the first importance in this connection. In such circumstances the publication of the present volume, in continuation of the one just mentioned, will naturally excite great interest and high expectations and it may be said at once that these are amply fulfilled. The book is divided into 3 sections, the first consists of a general résumé and forecast, in 3 chapters. Section II. contains an account of original investigations, in the period 1900–1905, consisting of abstracts of communications by various chemists, followed, in each case, by a critical examination of the matter and results from the point of view of the theoretical forecast of Section I. It is divided into (A) Reactions of Synthesis; (B) Reactions of Resolution and Decomposition. In Section III. is given an account of the technical progress in the cellulose industries and a general forecast of technological developments from the point of view of the matter of Section I. Additional bibliographical notes and 2 indices complete the volume.

Among the many excellences of the book three stand out in special prominence. The valuable criticisms of recent work, in Section II., not only help to place each research in its true perspective, but also suggest and inspire further investigations.

The authors possess, to an extent as rare as it is valuable, the admirable faculty of combining "pure" and "applied" chemistry. Although they never lose sight of the actual, or potential technological importance of a discovery, they are equally successful in keeping in constant view results which appear to be of purely theoretical interest.

Finally, a word of thanks and appreciation must be extended to the authors for their clear and most interesting style, qualities which, unfortunately, are far too rare in scientific books and papers.

The reviewer would like to quote from almost every page of the book in support of his commendations and in illustration of the authors' attitude towards their subject, perhaps the following extracts may be taken as typical ones: "Our main purpose is to establish, at a juncture which we consider to be critical, as it is favorable to progress, the definitely agnostic position which involves the recognition of current views of the constitution of cellulose as inadequate, reopens the matter from a more comprehensive point of view, and reduces all or any interpretations of the experimental quantitative facts to their present actual level of 'theoretical' anticipations of final generalizations. In the next place we desire to state the grounds for a considerable widening of the scope of the investigations which will be necessary for reaching such final generalizations of inclusive and exclusive value. There have been many attempts to solve the problem of the constitution of cellulose in terms of molecular formulæ. These essays postulate 'molecules' as the ultimate reacting units of cellulose, and generally extend the analogies of the 'molecular state' to bodies of this class without, we think, sufficient inquiry as to whether such methods of interpretation are really adequate" (Preface, p. vi.). " * * * cellulose is *essentially an aggregate*; the nature of this aggregate is a present definite object of investigation. It is by no means necessary that our ideas of discrete constituent molecular units apply to aggregates of this class. It is, as we know, generally stated that cellulose is a complex polymeride of a unit molecule of dimensions C_6, and of the general type of the carbohydrates, aldose or ketose. As a matter of fact, this view has not contributed to the progress of research, and its vagueness is seen

in the necessity for continually altering the dimensions of the supposed polymeride. Thus, in the case of the nitric esters, which have been more extensively investigated than any other group of derivatives, it has been found necessary to abandon the C_{12} formula (Eder) in favor of the C_{24} formula (Vieille), in order to avoid the formulation of nitrates representing fractional proportions of the assumed ultimate C_6, and later researches invalidate the assumption that the arbitrarily enlarged unit has any final value" (p. 5.) "Instances of this order can be multiplied to show that the progress of research in this (nitric) series of esters is obviously rendering the 'cellulose molecule' a function of the degree of refinement of experimental observations" (p. 45). "A general survey of cellulose technology produces the impression, as we have often had occasion to remark, of a high state of development of these arts, marked by extraordinary refinement of method and an accumulation of exact knowledge which, however, would scarcely rank as 'exact' by comparison with other branches of the science, or in the usual sense of the term as applied to scientific knowledge. We think this arises from the want of a theory, or generalization applicable to the cellulose groups, as to compounds in being, *i. e.*, in action and reaction" (p. 168).

The account given in Section III. of the book, of the present position and recent improvements in the manufacture of artificial silk and of the applications of viscose is brief, but admirably clear and interesting. One more quotation may be given to show the authors' general attitude: "It is not the purpose of this essay to formulate the many objectives of research in terms, nor to anticipate the results of such research. Our aim is to provoke discussion and generally to indicate directions of investigation, which we hope will be undertaken without regard to 'specialists' ' qualifications" (p. 174).

Messrs. Cross and Bevan have placed the chemical world under a decided obligation by the issue of their book and no person who is interested in chemical progress can afford to neglect reading it. J. B. T.

THE PRINCIPLES OF QUALITATIVE ANALYSIS, FROM THE STANDPOINT OF THE THEORY OF ELECTROLYTIC DISSOCIATION AND THE LAW OF MASS ACTION. By WILHELM BÖTTGER, Privatdocent in the University of Leipzig. Translated with the author's sanction and revised with his co-operation by WILLIAM GABB SMEATON, Instructor in General Chemistry in the University of Michigan. Philadelphia: P. Blakiston's Son & Co. 1906. pp. 300. Price, $2.00.

Since the introduction of the study of physical chemistry, and especially since the common acceptance of the theory of

electrolytic dissociation, many manuals of qualitative analysis, written avowedly in terms of the dissociation theory, have appeared in this country and abroad. An examination of most of these manuals shows that the changes from the older system are superficial and are generally confined to a brief exposition of the dissociation theory in the introduction, and reference to the precipitation of cations or anions instead of the precipitation of metals or acids, in the text.

This seemingly timid procedure was, however, based on sound reasoning. College students in America usually study qualitative analysis in their second year, in Germany and England in their first. A glance at most text-books of chemistry for undergraduates, written by avowed physical chemists, shows that the authors do not deem it advisable to teach much physical chemistry to the beginner; hence, the undergraduate is not prepared for a thorough application of physical chemistry to analysis.

Dr. Böttger addresses students who are prepared; he assumes that the student has studied Ostwald's "Principles of Inorganic Chemistry" and is studying Ostwald's "Scientific Foundations of Analytical Chemistry." For such students Dr. Böttger has written an admirable book. While special attention has been paid to the law of mass action and the dissociation theory, the author everywhere explains reactions in the light of modern general chemistry.

The book is also valuable for the many new tests for individual cations and for the excellent systematic method of testing for anions through the solubilities of the barium, lead and silver salts. The chapter on the rare elements also deserves notice as several new methods are introduced. Thus the book is not only interesting, but is a valuable practical manual. E. R.

LECTURE-NOTES ON CHEMISTRY FOR DENTAL STUDENTS. By H. CARLTON SMITH, PHG., Austin Teaching Fellow in Dental Chemistry and Lecturer on Physiological Chemistry at Harvard University Dental School. First Edition. New York: John Wiley & Sons. 1906. pp. 273. Price, $2.50.

The author states in the preface that the arrangement of this book follows rather closely the lecture course given by him at the Harvard Dental School. The book is divided into 8 parts, as follows: Qualitative Analysis, Dental Metallurgy, Volumetric Analysis, Microchemical Analysis, Organic Chemistry, Physiological Chemistry, Digestion, Urine. The task of presenting these subjects, except in a most superficial way, is certainly a hopeless one. The author emphasizes those mat-

ters which are of great practical interest to the dentist. Thus the subject of alloys and amalgams is considered at some length and the recent work of Black and others is presented. The subject of dental cements also receives detailed treatment and the composition of the various cements, including the recently introduced "Enamel Cement," or "Artificial Enamel," is given. Directions are included for a number of experiments to be performed by the student. These are inserted in the text.

The author's style is clear and concise and the book, as a whole, is satisfactory. A. S. L.

PORTLAND CEMENT. By RICHARD K. MEADE. Easton, Pa.: Chemical Publishing Co. 1906. 8vo. pp. viii + 385. Price, $3.50.

Among the several books published in recent years upon Portland cement, none will prove more useful than this volume by one whose personal experience and observation have been so intimately associated with that industry. This book is an enlarged and rewritten edition of the author's well-known "Chemical and Physical Examination of Portland Cement." It opens with an interesting chapter on the history of the industry, followed by a discussion of the chemical composition of cement. Under the head of "Proportioning the Raw Materials," are given the methods of calculating the quantities of limestone and cement rock or shale to be used, from the data furnished by analysis of the materials. Much labor is saved here by the use of graphical methods. In Chapter VII., on Kilns and Burning, is an especially good discussion of the chemical changes and the thermo-chemistry of the cement formation. The chapters of the methods of analysis, both of cement itself and of the raw materials, will have much interest to the general practicing chemist, as well as to those already engaged in cement works. Here are the schemes of cement analysis proposed by the Committee of the New York Section of the Society of Chemical Industry, and that proposed by the Committee of the Lehigh Valley Section of the American Chemical Society. The opinion is expressed that the latter will be more acceptable to those chemists engaged in cement mills, although greater accuracy is conceded to the former. Each is accompanied by valuable foot-note references, and there is a full discussion of both procedures. The "Physical Testing of Cement" is fully treated in Chapters XII.–XVII.; here are given the Standard Specifications reported by the American Society for Testing Materials, in June, 1904, and also a discussion of other methods. Since the standard specifications have been endorsed by

most of the associations and societies interested in the use of cement in this country, these methods will doubtless soon supersede all others. The book closes with a chapter on the Adulterations in Portland Cement, followed by an appendix and excellent index. FRANK H. THORP.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE, XXIII BAND. ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT FLÜSSIGEN METALLKATHODEN, VON DR. R. LUCION. Mit 181 in den Text gedruckten Abbildungen und 7 Tabellen. Halle a. S: Druck und Verlag von Wilhelm Knapp. 1906. pp. 204. Price, M. 9.

Dr. Lucion handles the story of the electrolysis of alkaline chlorides with a liquid metal cathode with the same thoroughness and mastery of the subject which has distinguished the other monographs of this admirable series.

In the first section he treats of the employment of mercury as cathode, and of the advantages and the difficulties connected with its use; he describes 50 patented processes employing the mercury cathode; he gives a historical review of the subject, calculations of experts on the financial side of the methods in practice, and tables of conductivity and specific gravity of solutions of potassium and sodium chloride.

In the second section Dr. Lucion discusses, in a similar manner, the methods employing a cathode of a metal in the fused state. Six processes of this type are described.

In speaking of the theoretical simplicity of the electrolytic methods of making chlorine and alkali hydroxides, the author refers to the expectation of some that in the future the carbonates will be made commercially from electrolytically made hydroxides; others seem to believe that hydrochloric acid will be made from electrolytic chlorine, and have patented processes for this purpose. The author points out the fallacy of such hopes, since thermo-chemical considerations show that it requires more energy to convert alkali chlorides into chlorine and alkali hydroxide, than it does to convert them into carbonate and hydrochloric acid. He says that the development of the electrolytic process depends on the demand of the market for chlorine, and as chlorine is in less demand than alkali hydroxides and carbonates, chemical methods for making the two last-mentioned products will continue in use.

Of the 50 mercury-cathode processes described, but 3 are at present in operation, the Solvay, the Castner, and the Kellner. The two last should be considered as one process, the Castner-Kellner, as the inventors have pooled their methods. The Solvay process is in use in Belgium and in Russia, the Cast-

ner-Kellner in England, Austria, and in the United States at Niagara Falls.

Of the 5 patented processes using a cathode of molten metal, that of Acker, using molten lead, is the only one which has proved a commercial success. The works are at Niagara Falls.

In comparing the 2 types, that with fused metal cathode has the advantage of the direct yield of fused alkali hydroxide instead of the aqueous solution of hydroxide in the mercury-cathode processes. It has the further advantage that the energy used is concentrated in a small space. In the Acker process a working unit, using 8000 amperes, 75 horse-power, and yielding 581 pounds (263.5 kilos) of sodium hydroxide per day is a comparatively small electric furnace with 4 carbon anodes. A Castner-Kellner cell, yielding 18 kilos of sodium hydroxide (after evaporation) per day and requiring 3.5 horse-power, is 6 feet long and 3 broad, and 14.3 such cells would be needed to furnish the product of one Acker unit. On the other hand, assuming the figures to be correct, the Castner-Kellner process would require just two-thirds of the energy per unit of hydroxide required by the Acker process.

The author says that economy in energy is by no means the only factor in a successful process, but he does not state definitely that one type is better than the other.

The book is excellently illustrated and printed. E. R.

A Text-Book of Sanitary and Applied Chemistry or the Chemistry of Water, Air and Food. By E. H. S. Bailey, Ph.D., Professor of Chemistry, University of Kansas. New York: The Macmillan Company. 1906. pp. 345. Price, $1.40.

This work resembles, in a general way, Lassar-Cohn's well-known book, "Chemistry in Daily Life." Its scope, however, is limited to those subjects which are of importance to the maintenance of health and to household economy. The book is divided into 2 parts. One part deals with the atmosphere, fuels, ventilation, lighting, water and its purification, sewage and sewage disposal, soaps, methods of cleansing and disinfection. Part II. deals with foods, beverages and accessories, food value and economy in dietetics. The author assumes that the reader has a fair knowledge of the rudiments of chemistry. The style, however, is clear and simple and is not unnecessarily encumbered with technical terms. Quite a large number of simple experiments are given in the text to illustrate the subjects under discussion.

There is great need for the dissemination of popular knowledge along these lines and we hope that the book will be well received. A. S. L.

COURS DE CHIMIE ORGANIQUE. Par FRED. SWARTS. Paris: A. Hermann. 1906. pp. 669. Price, $3.00.

This is an unusually clear and attractive book. Our French colleagues certainly have the power of clear presentation. It is usually a delight to read a French scientific book. This is a good example and the book can therefore be highly recommended to students and teachers. It is not at all exhaustive; it is rather elementary; so much the better. The Germans are the natural writers of exhaustive books. No one can do it as well, but when it comes to the matter of exposition the French are our masters.

There is one feature of the book that calls for mildly adverse comment. Wherever there are references to the literature, French authors are given precedence. To be sure, there are few references, but in most cases these are to French sources.

As an example of the author's power of clear presentation the chapter on the aromatic series (pp. 428–441) may be taken. The arguments are well stated and due attention is given to every suggestion of value that has been made regarding the constitution of benzene. The essential features of Thiele's theory of partial valences are well stated, and the improvement of the Kekulé formula that is brought about by the introduction of Thiele's conception is also fully recognized.

The discussion of hydrocyanic acid and the cyanides furnishes another good illustration of clear presentation. There is very little of the dogmatic in the author's treatment, though he appears to be a little more confident of the constitutional formula of potassium ferrocyanide (see page 161) than some of us are. In regard to the phenomenon of tautomerism as presented by the cyanides, he says: "It is not necessary to assume that KCN is a mixture of K—C≡N and of a small proportion of K—N≡C. This interpretation does not take account of the fact that the alcoholic iodides give only nitriles when they react with KCN. The most plausible explanation is to assume that KCN takes one or the other tautomeric form according to the reactions into which it enters. Further, this is equally true of HCN itself; but we have not yet isolated the two forms, either in the case of the acid or of the salts. The isolation of the two forms has been accomplished only in the case of the esters."

While the writer of this notice does not profess to have read the book through he has examined it pretty carefully, and has not come across anything that calls for censure. It is one of the most satisfactory books that it has been his pleasure to examine for some time. I. R.